CONTRACT REPORT NO. OST84-00012

D.S.S. Contract #12ST-23440-4-9029

DIRECT COAL LIQUEFACTION UNDER AMBIENT CONDITIONS

PHASE II

Optimization Studies on Solvent-Salt Liquid Clathrate Systems:
Approaches to Catalytic Upgrading

S. R. Stobart,
P. R. West,

Department of Chemistry,
University of Victoria,
Victoria, B.C.
April 22, 1985.

171 pp

OCT 1 1 1985
MICROMEDIA

SUMMARY

In Phase II of the study of application of solvent-salt liquid clathrate systems to low severity coal liquefaction, the principal objective has been to investigate catalytic upgrading of initially mobilized material in the clathrate phase.

To facilitate this objective, refinement and consolidation of the isolation and characterization methods of Phase I has been accomplished. Notably, mass balances of extractables and residues of 100 ± 5% have been achieved, and validated by spectroscopic monitoring. Under such conditions further good evidence of the physical nature of dissolution in the clathrate phase has been obtained by comparison with the classic solvent pyridine over an extended range of coal rank and temperature. Through examination of the vapour phase osmometric MW, thermal gravimetric analysis, nuclear magnetic resonance and elemental analysis it is clear that the aromatic solvent in the presence of a high ionic atmosphere mobilizes coal macromolecules by physical detachment from the coal mass.

Significantly, the total mobilization at readily accessible temperatures (140°C) for Devco bituminous coal (70% vitrinite, 85% reactives) of thirty per cent represents an attractive starting point for enhancement by upgrading reactions. The results of a preliminary examination of effects which may promote liquid clathrate extraction of coal, including addition of species which may act as upgrading catalysts, may tentatively be interpreted as follows: 1. Increasing dissolution accompanies increasing temperature in the range 100-140^{0}C;

2. Moderate pressures of added hydrogen gas (typically 500 psi) leads to enhanced coal mobilization; 3. Addition of organometallic additives e.g. $Fe(C_5H_5)_2$ or $Mn(C_6H_6)(CO)_3$ or use of clathrates based on derived organometallic cations at ambient hydrogen pressure appears to result in changes which are only marginal; 4. Addition of conventional hydrogenation (Rh) or hydrogenolysis (Ru) catalysts as trace additives leads to a modest increase in dissolution yields at ambient hydrogen pressure or at 500 psi; 5. Addition of sub-stoichiometric amounts of Lewis acids such as $TiCl_4$ has a beneficial influence on extraction characteristics which warrents further investigation; 6. Use of moderate pressures of added hydrogen at moderate temperatures markedly improves yields of dissolved material in a manner which suggests autocatalysis by agents in the coal-mass and which warrants further attention; 7. Addition of up to 50 mol% $AlCl_3$ to the $AlEt_3$-based liquid clathrates results in dramatic stabilization at elevated temperature which may be related to factors which are important in the design of air-stable liquid clathrates.

Paul R West

S. R. Stobart,
Professor.

P. R. West,
Associate Professor.

ACKNOWLEDGEMENTS

During the 1983-84 and 1984-85 Contract a significant direct contribution to the supervision and interpretation of the analytical data, in particular the gas chromatography and gc/ms studies was made by the analytical associate to the project, Dr. G. R. Branton, Department of Chemistry, University of Victoria.

Through direct participation in the experimentation, and through contribution of analytical facilities and expertise, Dr. W. M. Johnson, B. C. Ministry of Energy, Mines and Petroleum Resources has provided substantial assistance in the analysis of the complex products.

TABLE OF CONTENTS

Summary (i)

Acknowledgements (iii)

Table of Contents (iv)

List of Tables (vi)

List of Figures (viii)

List of Appendices (ix)

1.0 Introduction 1

2.0 Objectives of the 1984-85 Contract 7

3.0 Results 10

I. Characterization and Optimization of the Process 10

A. Introduction. The Experimental Procedures 10

(i) Centrifugation 13

(ii) Heavy Solvents-Tetralin Workup 14

(iii) Pyridine Solubility "Cross-Reference Experiments 15

(iv) Sonication 17

B. Comparative Studies 18

(i) Rank Dependence of Dissolution in Liquid Clathrate and Pyridine Solvent 18

(ii) Variation with Rank 24

C. Optimization of Yield From Dissolution of Coal in Liquid Clathrate Systems 26

II. Catalytic Upgrading in Clathrate Medium 30
1. Introduction 30
2. Progress during Phase II 33
3. Interim Conclusions 46

III Coal Structure: The Nature of the Dissolved Material 49
1. Introduction 49
2. Application of Arsenic Trichloride as an NMR Solvent for High Molecular Weight Coal-derived Materials 50
(i) Background 50
(ii) Application of $AsCl_3$ in obtaining ^1H and ^{13}C Spectra 52
(iii) Analysis of Spectra 52
3. Elemental Analysis of Coal Fractions 60
4. Vapour Phase Osmometry 62
5. Thermal Gravimetric Analysis 64
6. Volatile Components: Comparison by Gas Chromatography - Mass Spectrometry 65

4.0 Progress and Projection 69

LIST OF TABLES

Table 1.0 Solvent Reflux Yields vs. $\bar{R}_0$ 20

Table 2.0 Analytical Data of Coal Samples (%) 21

Table 3.0 Maceral Analysis 22

Table 4.0 Solubility (Solvent Class) Breakdown for Pyridine Reflux and Liquid Clathration of K-Seam and Devco Coals 23

Table 5.0 Effect of Temperature on Nominal Yield from Liquid Clathrate Solubilization 28

Table 6.0 Ashing of Fractions from Experiment 10 - 80 29

Table 8.0 ($C_5H_5Mn(CO)_3$) as Clathrate Additive in Experiments with Devco Coal 34

Table 9.0 Transition Metal Cation-based Liquid Clathrates 35

Table 10.0 Catalytic Hydrogenation Ability of $RuCl_2(PPH_3)_3$ in Liquid Clathrate Media 38

Table 11.0 Comparison of $RuCl_2P_4$ (100mg/run) and Control Experiments in Xylenes 40

Table 12.0 Comparison of $RhClP_3$ and Control Experiments 41

Table 13.0 Effect of Temperature and Catalyst at 500 psi H_2 Gas 43

Table 14.0 Effect of Lewis Acid Additive, 120°C/Xylenes/1 atm H_2 45

Table 15.0 Modified Brown-Ladner Analysis of NMR Spectra of Pyridine Soluble Material from KSeam and Devco Coals 57

Table 16.0 ^{1}H and ^{13}C NMR Data 58

Table 17.0 Elemental Analysis 61

Table 18.0 Subdivision of Pyridine Soluble Fractions from Clathrate on Sephadex LH20 63

LIST OF FIGURES

Figure 1.0	Schematic Representation of Liquid Clathrate Extraction	3
Figure 2.0	Coal Extraction by Refluxing Pyridine and by Tetra-n-propylammonium Triethylaluminium Clathrate	25
Figure 3.0	^{1}Hmr Pyridine Soluble Fraction 10-9-B (Acid Washed) d-5 Pyridine 60 Mhz TMS	53
Figure 4.0	250 Mhz ^{1}Hmr Spectrum Pyridine Soluble Fraction 10-29B Arsenic Trichloride	54
Figure 5.0	^{13}C 250 Mhz NMR Spectrum Pyridine solubles 2-47B Arsenic Trichloride	55
Figure 6.0	Gc/ms: Sample 10-42-1-1 Toluene Layer Solubles Methane CI Devco Coal Clathration	67
Figure 7.0	Gc/ms: Sample 10-11-1-1 Toluene Fraction Devco Coal Pyridine Reflux	68

APPENDICES

I Results

I-1 Results of Application of Liquid Clathrate to Selected Coals -70-

I-2 Nuclear Magnetic Resonance Spectra in $AsCl_3$ and d-5 Pyridine -81-

I-3 Thermal Gravimetric Analysis Results -89-

I-4 Elemental Analaysis of Coals and Coal Extracts -96-

I-5 Gas Chromatograms and Tables of Volatile Components -101-

II Experimental Methods

II-1 Clathration Procedures -120-

II-2 Methods for Quenching the Coal/Clathrate System and Separation of Materials -125-

II-3 NMR Measurments: Use of Arsenic Trichloride as a Solvent -130-

II-4 Preparation of Samples for Molecular Weight Determination -132-

II-5 Determination of Molecular Weight by Vapour Phase Osmometry -134-

II-6 Gc/ms: Sep-Pak Fractionation of Coal Liquids -138-

II-7 Synthesis of Transition-Metal Complexes -141-

II-8 Removal of Solvents by Vacuum Distillation: Purifying and Drying of Solvents -144-

II-9 Measurement of Loss on Ignition -151-

II-10 Inert Atmosphere Glove Box Operations -152-

III Other

III-1 Review of Objectives -153-

III-2 Brown-Ladner Analysis -155-

III-3 References - Application of $AsCl_3$ Solvent -159-

1.0 INTRODUCTION

Reduced Severity Liquefaction - An Overview

In the present (1984-85) climate of lowered conventional fuel sosts, strategic research on coal conversion has focussed on the discovery of favourable solvent-catalyst (chemical) combinations for mobilizing and depolymerizing the extended aromatic (arene) networks of the coal mass. In each instance the object is to overcome the punitively adverse thermodynamic and technological problems that are known to exist for high temperature coal hydroliquefaction processes.

In contrast, low severity processes lack the thermal energy for C-C and C-O bond cleavage (available at >400°C and must ultimately rely on catalytic reduction processes to achieve liquefaction.

Most novel reduced temperature and pressure innovations have explored direct chemical reaction as the principle driving force in the depolymerization (or net solubilization) processes including extensive work on acid (1) and superacid (2) processes, the latter including hydrogen donors and hydrogen overpressure. Other notable approaches have been oxidative, principally the work of Deno et al (3), or carbonionic alkylation routes (inherently reductive), for example, as explored by Hardy and Stark (4).

The Liquid Clathrate Concept

The present programme stems from the discovery of a powerful novel two-phase solvent system by Professor J. L. Atwood of the University of Alabama.

Certain main group and potentialy catalytic transition metal salts dissolve in aromatic solvents (toluene, xylene) to form highly ionic polar liquid clathrate phases that have the novel property of co-exisiting with the pure solvent phase.

Such liquid clathrate systems have the capability for dissolving significant coal solid and heavy bitumen under low temperature conditions with the added advantage of contually stripping the oil and asphaltene fractions into the co-existing collector phase.

Indeed conceptually, the process can be presented quite simply, Figure 1.0. It is important to note that physical dissolution is intended in the primary transfer from coal solid to clathrate phase, and that macromolecular fragments with significant hydrogen deficiency will be present in the clathrate.

Subsequently a catalyst or chemical agent present as a dissolved salt or integral element of the clathrating medium must effect useful upgrading of the macromolecules under moderate conditions of temperature and hydrogen overpressure as indicated in the diagram.

The background of liquid clathrate behaviour has been included in other reports and presentations (5,6) and it will suffice to present a summary of the scope of the phenomenon and the background of the discovery of its application to coal liquefaction.

As part of a general study of compounds related to so-called Ziegler-Natta catalysis, Ziegler and coworkers reported in 1960 the synthesis of compounds of the type $M[Al_2R_6X]$ according to Equation (1).

$$2AlR_3 + MX \rightarrow M[Al_2R_6X] \qquad (1)$$

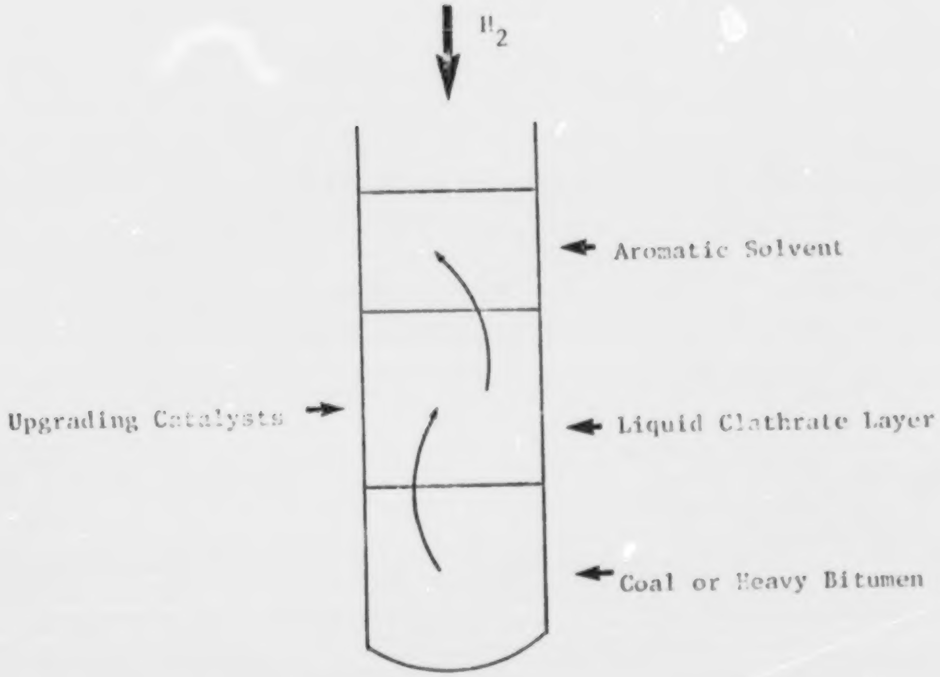

H_2
Aromatic Solvent
Upgrading Catalysts
Liquid Clathrate Layer
Coal or Heavy Bitumen

Figure 1.0.

On attempting to dissolve $K[Al_2Me_6N_3]$ in benzene, J. L. Atwood found the material dissolved quickly, and two liquid layers were observed. Subsequently the scope of Equation (1) was rapidly expanded and the liquid-layering effect was obtained for virtually all combinations of M, X, and R, e.g. Table 1.

Table 1. Components of the $M[Al_2R_6X]$ Parent Compound

M	R	X	
Na^+	$-CH_3$	F^-	$HCOO^-$
K^+	$-C_2H_5$	Cl^-	NO_2^-
Rb^+	$-C_3H_7$	Br^-	O_2^-
Cs^+	$-C_4H_9$	I^-	OH^-
NR_4^+		N_3^-	SO_4^{2-}
PR_4^+		SCN^-	CO_3^{2-}
$(C_6H_6)_2Cr^+$		$SeCN^-$	O^{2-}
$(C_5H_5)_2Co^+$		NO_3^-	
Ba^{2+}		CH_3COO^-	

By n.m.r. spectroscopy, it has been established that the lower clathrate phase for $K[Al_2Me_6]N_3$ has 5.8 benzene molecules per ion pair.

While the original term clathrate had been restricted to solids, the novel properties of the ionic phases led Atwood to coin the phrase "liquid clathrates". Some of the most important properties are as follows:

(1) The behaviour is observed only in aromatic solvents.

(2) All of the parent compound is confined to the lower layer.

The upper one contains only the excess aromatic.

(3) For a given set of M, X, R, and aromatic the lower layer will only load a given constant amount of aromatic, referred to as the A/A (aromatic-to-anion) ratio.

(4) The aromatic is trapped by, not bonded to the parent compound and may be freed in some cases by a small change in temperature.

The phenomenon is not restricted to the complex aluminates but has been observed for silazides of the structure $Na^+[NSi(Me)_3]^-_2$ provided the sodium ion is complexed by a crown ether.

Interest in the use of liquid clathrate extraction was sparked by Atwood's observation that on contact with <100 mesh Mary Lee Seam Alabama coal, the clathrate phase immediately darkens, and transfer to supernatant toluene is evident.

Atwood reported that approximately 20% of the coal solid was mobilized in the clathrate phase on exposure to the clathrate at a ratio of 10 ml of liquid phase to 1 g of coal that had been dried by heating at 110°C for 24 hours. The azide salts employed in these studies lend themselves to separation from the clathrate phase by fractional crystallization. Subsequently yields were determined by distillation of the organic material in the solvent and clathrate phases.

References

1. L. J. Darlage and M. E. Bailey. Fuel 55, 205-210, (1976) and references therein.
2. G. A. Olah, M. R. Bruce, E. H. Edelson and A. Husain. Fuel 63, 1130 (1984).
3. N. C. Deno, K. W. Curry, A. D. Jones, K. R. Keegan, W. G. Rakitsky, C. A. Richter and R. D. Minard. Fuel 60, 210 (1981).
4. C. I. Hardy and L. M. Stock. Fuel 61, 701 (1982).
5. Coal Liquefaction at Low Temperature and Pressure. S. R. Stobart, P. R. West and J. L. Atwood. In Proceedings of the Coal Liquefaction Contractors Review Meeting, November 8-9, 1982, Ottawa, J. F. Kelley, editor, p. 251.
6. J. L. Atwood. Rec. Devel. Sep. Sci. 3, 195 (1977).

2.0 OBJECTIVES OF THE 1984-85 CONTRACT

Initially a programme of work on application of the liquid clathrate system to Canadian Coals was proposed to encompass the three principal areas of investigation detailed below. In the following Results Section, progress in these areas will be reported.

I. CHARACTERIZATION AND OPTIMIZATION OF THE PROCESS

While early work by Atwood had indicated the utility and overall mobilization of a series of Alabama and other U.S. coals, the undifferentiated distillation workup did not allow accurate estimation of the nature of the initially dissolved material.

Accordingly a workup procedure based along classic solvent separation lines was required to facilitate spectroscopic and other analysis of the products, and to permit more precise measurement of yields. Mass balance and effects of temperature, solvent and other process parameters could then be easily measured.

Though significant progress was made in Year I (see Contract 25ST-23440-2-9100 Final Report), substantial refinement of methods particularly in the area of mass balance has been made, and is reported herein.

II. LIQUID CLATHRATE-CATALYST APPLICATIONS

Following optimization, the second year programme has been vitally concerned with net upgrading (hydrogenation) in the clathrate phase as a means of increasing yield and reducing the average molecular weight of the dissolved material.

Clearly the stability, efficiency and mode of action of both homogeneous and heterogeneous catalysts in the clathrate system represents a new area of research. Accordingly systematic approaches to the upgrading problem have focussed on known homogeneous hydrogenation catalysts based on Ru and Rh in the first instance, with an emphasis on variation of both hydrogen pressure and the possible effect of Lewis acid stabilizers (promotors) in the process.

Early in the contract period, more general survey reactions employing transition metal complexes both as an integral part of the clathrate salt, and as neutral additives were subjected to renewed scrutiny, as reported in the Results Section.

III. COAL STRUCTURE: THE NATURE OF THE DISSOLVED MATERIAL

Given the low severity of the process (Room temperature → 180°C), the clathration approach offers a fresh new route to the study of the spectroscopic and chemical properties of coal derived macro molecules.

In the current contract year, an emphasis on selected techniques (VPO, elemental analysis, TGA, nmr) has been indicated, with application to the high molecular weight preasphaltene material that constitutes the bulk of the initially dissolved material.

While the foregoing represents a synopsis of the objectives of the Contract as detailed in the work statement, a re-iteration of the overall objectives of the project is contained in Appendix III-1.

3.0 RESULTS

I. CHARACTERIZATION AND OPTIMIZATION OF THE LIQUID CLATHRATE LIQUEFACTION APPROACH

A. INTRODUCTION: THE EXPERIMENTAL PROCEDURES

In the programme, liquid clathrates based on triethylaluminum and a range of complexing salts (mainly tetra-n-propyl ammonium iodide) were used, principally in toluene or mixed xylenes as solvents, though a number of high temperature experiments were attempted in tetralin.

Though not a usual format, it seem instructive to include the simple preparation of the Liquid Clathrate in this Introduction to demonstrate the ease of forming the novel solvent system:

Preparation of Liquid Clathrates

Material routinely used for coal extractions was made in about 500 ml batches. 100 g of NPr_4I (0.319 mole) was placed in a 1000 ml Erlenmeyer flask and transferred to the inert atmosphere glove box. 500 ml of distilled toluene (stored over molecular sieves) was poured over the salt and 87 ml (0.638 mole) of $AlEt_3$ was slowly added. Following mixing for 5 minutes approximately 500 ml of liquid clathrate formed and all the NPr_4I dissolved. The Erlenmeyer was stoppered and the liquid clathrate stored in the inert atmosphere glove box until needed. The liquid clathrate was stable indefinitely under these conditions.

Subsequently the desired weight of coal is treated with clathrate under specified conditions of temperature and hydrogen overpressure, with added catalyst or stabilizer (for example $AlCl_3$). The details of the experimental procedures are contained in Appendix II-1.

Examination of Appendix I-1 shows results of each successful liquefaction procedure conducted during the Contract year. Runs abandoned due to experimental error, usually loss of mass balance are not included. Particular elements of Appendix I-1 are reprised as necessary, for example, in discussion of catalytic experiments.

The presentation of the data in terms of solubility in aromatic solvent, chloroform and pyridine, reflects the workup procedure. The experimental details of the isolation are provided in Appendix II-2.

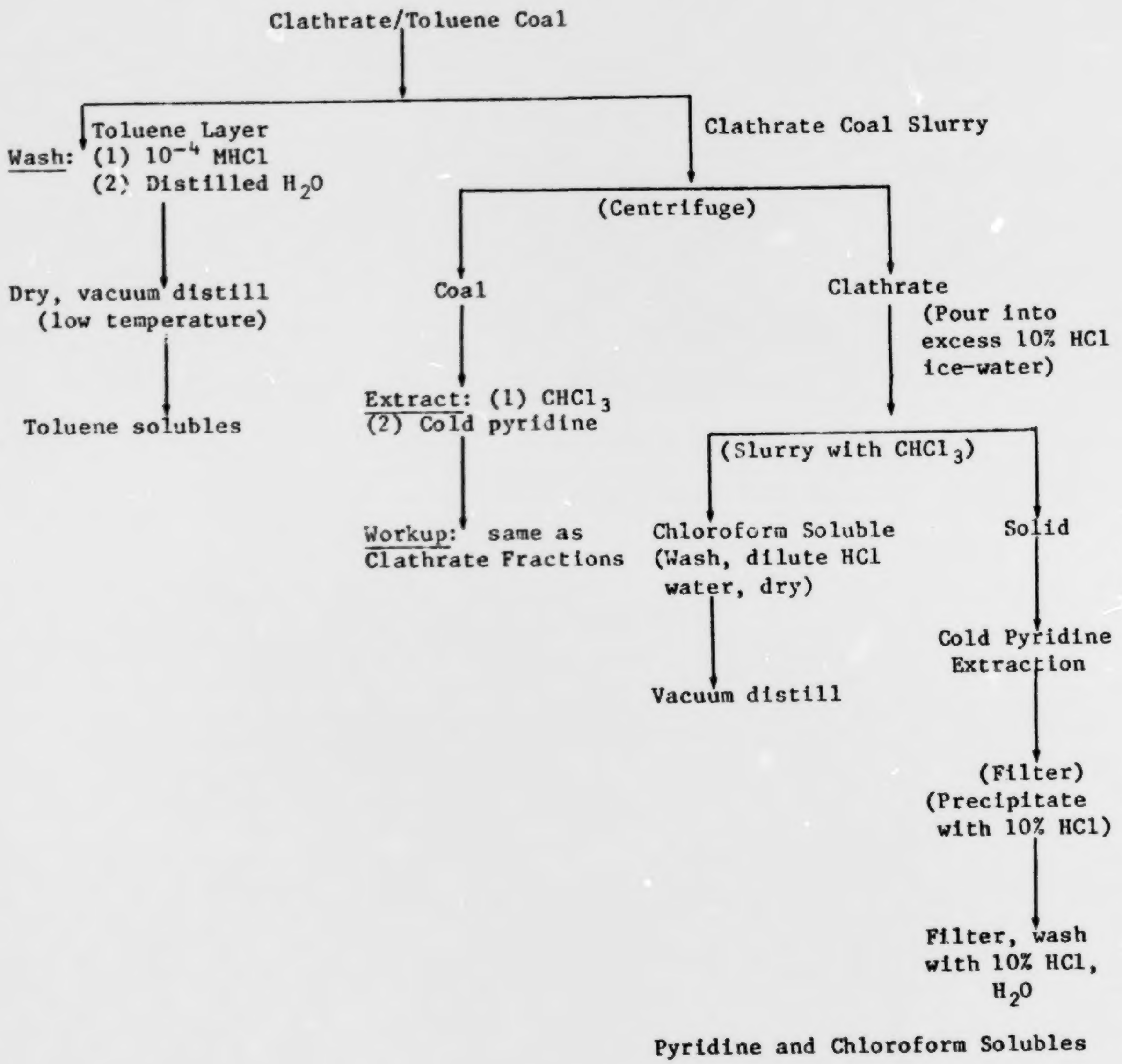
Overall, the separation is shown (for toluene as solvent) in Scheme 1, overleaf. It should be noted that a significant change in the isolation of pyridine solubles has been made from Year I, namely precipitation rather than distillation of the pyridine extracts. A notable uncertainty at the end of the first year of the study was the lack of mass balance, often ranging up to 110-120% of the nominal coal charge. It was discovered early in the second contract year that substantial entrainment of pyridine hydrochloride in the final (pyridine soluble) pre-asphaltene fraction had occurred. The source was deduced to be hydrogen chloride entrapment in the filter cake *prior to pyridine extraction*. Pyridine hydrochloride was then formed and retained throughout the following distillation workup.

As a general point, it can be recommended that:

(1) Care be used in avoiding salt formation for any pyridine extraction of a coal residue that has been treated under acid conditions.

(2) Routine monitoring of pyridine extracts by nmr spectroscopy be made using an alternative solvent (*i.e.* not d-5 pyridine). It is

SEPARATION SCHEME



SCHEME 1.

recommended that either CS_2 or $AsCl_3$ as developed in present work [Results Section III, 1.] be used.

The nature of the results presented in the Tables of Appendix I-1 can be summarized simply: The aromatic phase (toluene, xylene, tetralin) designated A provides both "oil" (pentane or hexane soluble) and "asphaltene" (aromatic soluble) material. The cold pyridine extraction of the residue (B) and clathrate mobilized material (C) has been equated with the preasphaltene fraction defined for high temperature liquids. The latter pyridine material is decreased by the fraction that is chloroform soluble, a division dictated by the workup procedure. Several experimental aspects of the separations that have been examined in the current contract year emphasize the inherent physical (solvent) separation that is initially effected by the clathrate:

(i) Centrifugation:

For extraction of the product from heavy (salt) media like the clathrate phase, it has been found necessary to collect coal fines by centrifugation in order to assess the mobilized material in the clathrate. Accordingly the slurry (clathrate phase and coal residue) is transferred to centrifuge tubes under nitrogen, and the tubes are covered with septum caps in the subsequent centrifugation. In 70°C, toluene experiments, the substantial clathrate unsoluble fraction observed by Year I procedures was reduced to *ca* 80 mg by this procedure.

Notwithstanding, prolonged ultracentrifugation would undoubtedly result in further sedimentation. Ultimately, however, it would be difficult to assign the solid removed specifically to coal fines since precipitation through deterioration of the clathrate phase, the sharply reduced temperature and regressive reactions would become important.

In summary, a gradation of molecular weights is assumed to exist in the clathrate phase including colloidally dispersed material and fine particles.

It is important to note that coal subdivision will be increased both by solvent action and by mechanical effects.

To determine any effect of the clathration process on particle size, 8.4 g of K-seam coal sized to pass a 60 mesh screen but not an 80 mesh screen (-60, +80) was put through the standard 20 hr clathration reaction. When the reaction was terminated, the coal residue was washed (without being stirred in pyridine), dried and then sieved through 80 and 100 mesh screens. The results showed that 91% of the residue passed through the 80 mesh screen and 78% passed through the 100 mesh screen. A control experiment without the clathrate by stirring in toluene for 20 hours showed that after stirring 90% of the residue passed the 80 mesh screen and 88% the 100 mesh screen. These results indicate that the particle size reduction was a mechanical effect.

(ii) Heavy Solvents - Tetralin Workup

Clearly the use of recycle and other high molecular weight solvents (hydrogenated anthracene oil) will present particular difficulties. Modifications were necessary for the use of tetralin as a solvent, and several initial runs were abandoned due to mass balance problems.

The following approach was used:

First, vacuum distillations of the tetralin solubles (A layer) are required. Secondly, significant tetralin invades the chloroform and pyridine soluble fractions and is not removed by the workup. Final removal has been accomplished by backwashing all fractions with pentane after their isolation. Yields are reduced by the extent of light oil production (pentane extracts are significantly coloured).

(iii) Pyridine Solubility "Cross Reference" Experiments

As an element of the extension of the coal rank dependence survey initiated in Year I, several experiments designed to assess the inherent solvent power of the clathrate phase have been conducted throughout the contract year. In particular we have been interested in the nature of the material dissolved by the clathrate on the one hand, and classical solvents (especially pyridine) on the other.

The following section III-B (page 18) presents a summary of the comparative data that establishes the apparent parallel in terms of rank between the clathrate and pyridine phases, and serves to clearly define the liquid clathrate as a powerful physical solvent rather than as a chemical agent. Much of this comparative data was presented at the Coal Contractors Conference in Calgary, November 14-16, 1984.

Additional experiments providing corrobative evidence for the physical dissolution process were conducted during the contract year as a vehicle to refining the experimental procedures and confidence in the results:

(a) Solubility of Pyridine Reflux Product in Clathrate

A test was run to determine the extent to which pyridine-soluble coal material was solubilized in clathrate. This involved clathrating 1.78 g of HCl-precipitated pyridine reflux extract of Devco coal at 85°C for 20 hours, centrifuging and determining the amount of residue which was centrifuged. This amounted to a total of 0.043 g or 2.4% clathrate-insoluble (see Experiment 10-36, Appendix I-1).

(b) Clathrate Solubility of High Temperature Liquefaction Products

Two 10 g samples of Devco and of K-seam coal were taken to the B.C. Research facilities and liquefied at 400°C for 25 minutes under 3000 psi of H_2 in tetralin. The material was washed out of the reaction containers with toluene and brought back to these laboratories and one sample of each was filtered. The filter cakes were clathrated using standard techniques. The 5.29 g of Devco filter cake gave 3.09 g of soluble material of the clathrate layer. The 5.02 g of K-seam filter cake gave 3.73 g of soluble material. Both fractions had higher than usual pyridine insoluble material in the "supernatant" and the chloroform and pyridine soluble portions in the K-seam fraction were much higher than in the corresponding Devco fraction (see Experiments 17-3 and 18-3 in Appendix I-1). It was evident that the clathrate dissolved approximately the same amount of the filter cake as did pyridine (see Experiments 17-2, Devco; 18-2, K-seam).

(c) Clathration of Pyridine Insoluble Coal Fractions

In order to extend the work designed to determine if clathration renders additional material soluble subsequent to extraction of the coal by pyridine, the pyridine insoluble portion from a refluxing of Devco coal was clathrated and worked up. As can be seen in Experiment 10-32 in Appendix I-1, 3.51 g of pyridine insoluble coal residue gave an additional 0.281 g of soluble material after clathration.

(iv) Sonication

It seemed advisable in view of literature reports of improved solvent extraction efficiency to determine whether improvements in either the basic clathration experiment or workup could be achieved by carrying out the operations in a simple sonication bath using water as the medium.

An experiment was run to evaluate the effect of sonicating the chloroform-insoluble portions of the clathrate and coal residues with pyridine rather than stirring them. The results shown in Experiment 10-30 in Appendix I-1 indicate that there is a slight enhancement in the amount of pyridine soluble material from the residue fraction but more work is required to confirm this.

Another experiment was run in which the reaction was agitated using sonication rather than mechanical stirring. The mixing of the layers observed in the standard experiments was not seen in this one and, as the figures in Experiment 10-31 in Appendix I-1 show, the extraction is significantly poorer.

B. COMPARATIVE STUDIES:

(i) RANK DEPENDENCE OF DISSOLUTION IN LIQUID CLATHRATE AND PYRIDINE SOLVENT

Following the thorough refinement of workup procedures and achievement of appropriate mass balances, as reported in the last section, it was possible to accurately assess solvent and liquid clathrate extraction.

The yields for the obvious options - refluxing toluene b.p. 110°C and refluxing pyridine b.p. 118°C are shown in Table 1.0 for a series of coals of differing rank. Special emphasis in the clathrate experiments has been placed on two of these coals: "K-seam", the medium volatile A bituminous Cretaceous coal from Fording Coal in British Columbia, and Devco, the Nova Scotian coal with higher sulphur characteristics of these eastern (Carboniferous) coals. Analytical data for a range of coals used in the comparative study are shown in Table 2.0. It will be noted that a number of the coals used are the same as reported in 1983-84, but yields are now based on good nominal mass balances and the comparison is made at ca 120°C for both pyridine and clathrate extraction. Maceral analysis was obtained for a number of target (and B.C. coals) and while variations are evident, the K-seam and Devco bituminous coals are comparable in vitrinite, but the internite/semifusinite content of the K-seam (Cretacous coal) is somewhat higher as is always found, Table 3.0.

In Table 4.0 the pyridine soluble material has been broken down into a toluene soluble fraction and residual pyridine soluble material.

The data was obtained by simple sonication in toluene of the raw pyridine soluble product obtained by precipitation with HCl in the same manner as the clathrate phase workup, Scheme 1. Note the rather higher yield of toluene soluble material by this indirect route than by direct reflux with toluene, a phenomenon likely related to physical swelling of the coal by pyridine freeing additional asphaltene material from the solid matrix. Incidentally, the solubilities are rather lower than some literature reports. For example, pyridine reflux solubities of Illinois 6 as high as 23% have been reported, though in our hands only 12% was obtained by reflux and precipitation. We find extensive washing with dilute HCl is necessary to remove residual solvent even employing precipitation for these reflux experiments as well. Moreover, the yields reported are those for simple filtration (Whatman 40 paper) and woud be doubtless further reduced by either micropore filtration or ultracentrifugation.

Table 1.0. Solvent Reflux Yields vs. $\bar{R}_o$

Coal	Toluene Reflux %	Pyridine Reflux %	% Ash	Corrected Reflux %	$\bar{R}_o$	Clathrate % (daf)
Forestburg	0.18	3.0	--	~3	<0.4	NEG
Merritt	0.57	4.3	21.2	5.5	0.82	-
K-seam	0.85	13.7	3.4	14.2	0.90	15.0
Devco	0.26	20.5	~7.0	21.7	0.92	21.0
Mary Lee	0.17	21.4	13.6	24.8	0.94	24.0
Balmer Low[2]	--	6.3	9.0	6.9	1.17	9.6
Balmer High[2]	--	2.6	9.3	2.9	1.33	7.7
Canmore	negligible		--	--	>2.28	NEG

[1] Clathrate yields are in the combined perentage for all solvent fractions, compared at 118°C (temperature of refluxing pyridine) for 18 hour extraction. Correction for ash content has been made.

[2] The Balmer samples differ in the $\bar{R}_o$ values.

Table 2.0. Analytical Data of Coal Samples (%)

Coal	C	H	N	S	Ash	Moisture
Hat Creek	45	2.8	0.7	0.39	26.6	23.5
Quinsam I	71.49	4.48	0.92	0.39	11.33	4.01
Devco	73.24	4.65	1.57	1.69	6.83	2.86
K-Seam	81.38	5.04	0.8	0.75	3.45	1.50
Forestburg	58.63	3.71	1.26	0.50	7.48	10.0
Quinsam II	69.23	4.75	0.88	0.38	10.15	3.66
Mary Lee	68.82	4.63	--	--	13.67	0.82
Canmore	86.64	3.62	--	--	--	--
Merritt	63.70	4.51	--	--	21.2	1.67

Table 3.0. Maceral Analysis.

	Vitrinite		Liptinite		Inertinite		Semi-fusinite		M.M.		Total Counts
		%		%		%		%		%	
Devco	331	66.2	95	19.0	31	6.2	10	2.0	33	6.6	500
Granby	127	25.4	42	8.4	8	1.6	1	0.2	322	64.4	500
Mary Lee	331	66.2	53	10.6	29	5.8	-	-	87	17.4	500
Quinsam	339	67.8	71	14.2	47	9.4	21	4.2	22	4.4	500
Telkwa	289	57.8	112	22.4	--	--	7	1.4	92	18.4	500
Merritt	226	53.2	127	25.4	1	0.2	7	1.4	99	19.8	500
K-seam	327	65.4	55	11.0	65	13.0	42	8.4	11	2.2	500
K(Fording) (average)		72.6		4.3		6.6		12.4		4.1	
K_A(Grieve)*		73.7		3.4		3.6		13.8			
K_B(Grieve)*		71.7		4.0		2.8		21.0			

*As per Dr. D. Grieve, B.C. Ministry of Energy, Mines & Resources.

Table 4.0. Solubility (Solvent Class) Breakdown for Pyridine Reflux and Liquid Clathration of K-seam and Devco Coals.

		Toluene Soluble	Chloroform Soluble	Pyridine Soluble[2]	Total daf
Devco[1]	A. Clathration	1.9	4.1	15.0	21.0
	B. Pyridine Reflux	3.0	--	17.2[3]	21.7
K-seam	A. Clathration	1.6	2.6	10.8	15.0
	B. Pyridine Reflux	2.7	--	7.0	9.7[4]

[1] Overall recoveries approach 93%. 10% HCl dissolves 7 weight percent of Devco coal on reflux, potentially carbonate mineral matter.

[2] Cold pyridine extraction. For Devco coal, the coal residue yields only 2% of these pyridine solubles.

[3] Sonication in chloroform dissolves 9.6% of the pyridine soluble material = 1.65%.

[4] An unusually low value. Previous reflux yields were in 14% range.

In summary, several features are evident:

(1) The toluene solubility, i.e. without clathrating salt is predictably extremely low.

(2) The overall net yield (both extractions ca 120°C) for clathrate and solvent are similar.

(3) In favourable cases (Devco) a substantial fraction >20% of the coal is mobilized.

We suggest that the data is fully consistent with the following conclusions:

(i) The liquid clathrate phase is functioning as a solvent in a strictly physical sense.

(ii) Its efficiency for the two principal target coals (K-seam and Devco) does not differ from the classical near optimum solvent pyridine.

(ii) VARIATION WITH RANK

Classical solvents usually exhibit a maximum dissolution of the coal solid near 85%C daf. Examination of Figure 2.0 shows that in our hands the rank dependence of the clathrate media does not differ significantly from pyridine. Accordingly both coals of low rank such as Forestburg and a Canmore anthracite provide small to negligible yields of soluble material on prolonged extraction.

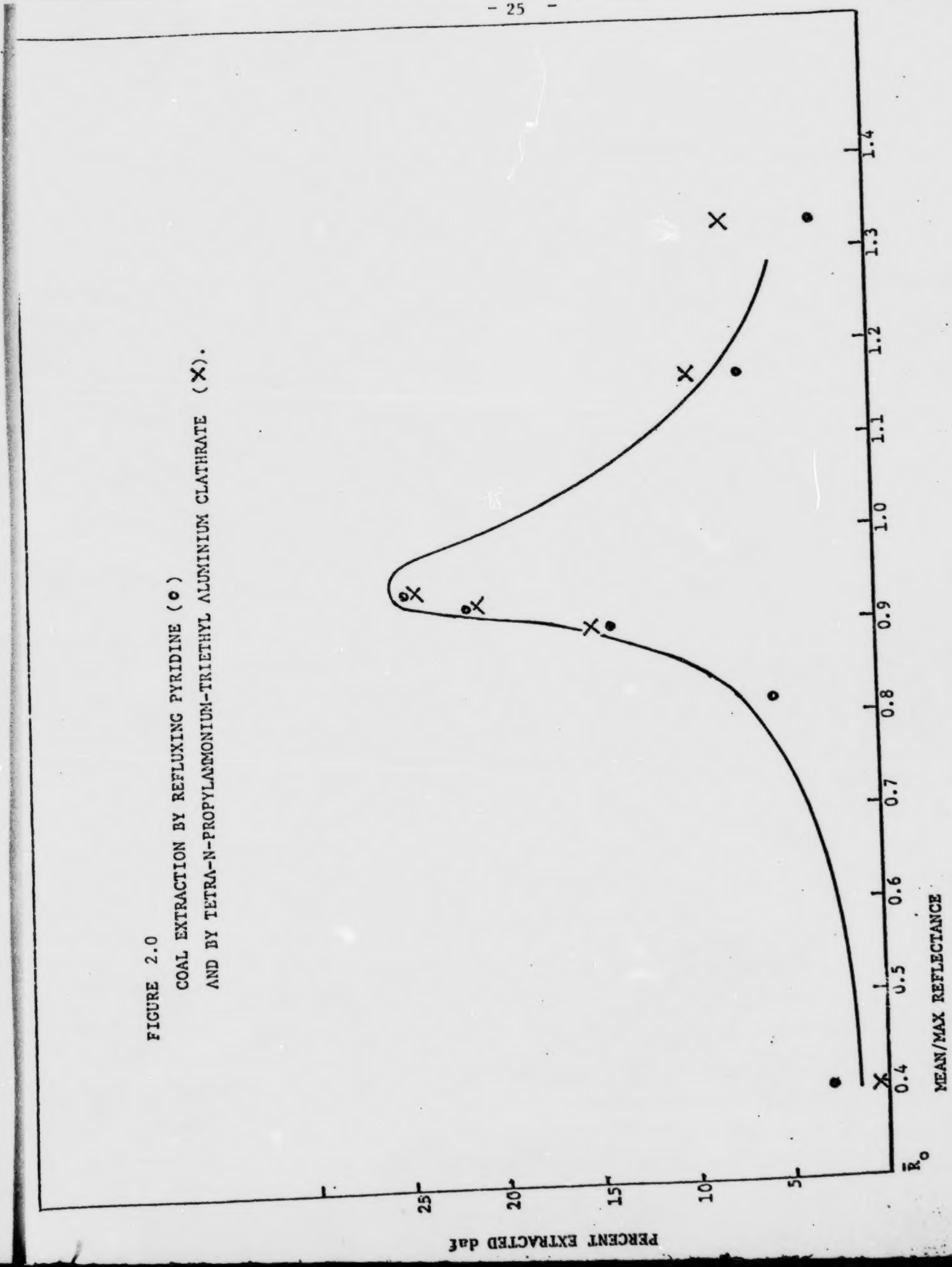


FIGURE 2.0

COAL EXTRACTION BY REFLUXING PYRIDINE (●)

AND BY TETRA-N-PROPYLAMMONIUM-TRIETHYL ALUMINIUM CLATHRATE (X).

C. OPTIMIZATION OF YIELD FROM DISSOLUTION OF COAL IN LIQUID CLATHRATE SYSTEMS

The focus of the work in the present contract year was concentrated on exploration of catalytic upgrading particularly in the latter part of the year. A full review of these experiments is presented in the following section.

However, several other parameters were studied, and data is reported in the Appendix I-1 tables. In particular preheating the coal to ca 300°C in oxygen free nitrogen was examined (Appendix I-1, table I-1-5, Experiments 10-40 (Devco) and 2-58 (K-seam)). No significant enhancement was observed.

Demineralization of a coal sample with 10% HCl, for example 10-41, Table I-1-5 showed no significant effect, but since the control and this experiment were conducted in the absence of hydrogen, the experiment cannot be viewed as an adequate test of autocatalysis particularly in view of the most recent data discussed in Results, Section II following.

Effect of Temperature. Higher Boiling Solvents.

Modest increases in temperature to 120-140°C, particularly in the presence of an overpressure of H_2 gas have revealed yields based on reasonable mass balances that a fall within the range projected for clathrate efficiency namely 30-35% daf. It should be noted that these observations are made in the absence of external catalysis, but leave open the intriguing possibility of a catalytic role for the natural mineral matter in the coal. Table 5.0 below shows the progression in yield with temperature recorded in the present contract, both including and excluding non-centrifugeable material in the clathrate phase that is insoluble in pyridine.

Two points relative to yields from Devco coal should be made:

(i) The maximum recovery is 93% (7% solubility of the coal in 10% HCl has been established).

(ii) Ashing studies have been conducted on the pyridine insoluble material in the clathrate phase. As shown in Table 6.0 below, only a trace of ash is found in this material indicating that it has been mobilized.

NOTE:

Significant Figures: Variability in Clathrate Yields

While the data in Tables 6.0 and 7.0 is reported to several decimal places, and the yields in Appendix I have a similar highly accurate appearance it should be noted that at any given temperature overall yield can vary ± 1.5 per cent.

Given the high degree of subdivision into fractions in the workup procedure with all data being recovered gravimetrically, consistency of the results is considered to be comparable to model high temperature studies conducted here and elsewhere.

Table 5.0. Effect of Temperature on Nominal Yield from Liquid Clathrate Solubilization.

Devco Coal: 20 hours.

	Temp.	Solvent/ Conditions	Total Solvent % Soluble	Total Clathrate % Soluble	Mass Balance
10-38	70°C	Toluene	14.08	14.68	96.6
10-37	85°C	Toluene	16.70	18.68	98.6
10-44	100°C	Toluene	18.25	19.66	101.0
10-47	120°C	Xylenes	20.66	21.50	88.3
10-50	120°C	Xylenes*	19.50	24.11	92.0
10-75	120°C	Xylenes (500 psi H_2)	21.43	24.16	103.5
10-80	140°C	Xylenes. ARGON	23.68	26.20	100.9
10-82	140°C	Xylenes (500 psi H_2)	29.20**	35.52	105.0

Solvent Soluble = Cold Pyridine + $CHCl_3$ + Aromatic

Clathrate Soluble = Solvent Soluble + Pyridine Insoluble Fraction from Clathrate Phase

*Two aliquots of clathrate.

**Exhaustive (2 x 20 hr extractions) with pyridine at 140°C under H_2 gave 28.0% soluble.

Table 6.0. Ashing of Fractions from Experiment 10-80.

	Wt. Crucible	Crucible + Sample Before Ashing	Crucible + Sample After Ashing	Wt. Sample Before	Wt. Sample After	% Left	% Lost
10-80B cp sol	9.7532	10.0815	9.7549	0.3283	0.0017	0.5	99.5
10-80B cp insol	9.8071	10.3131	9.8273	0.5060	0.0202	4.0	96.0
10-80C cp sol	9.5841	9.8954	9.5842	0.3113	0.0001	0.0	100.0
10-80C cp insol	9.6311	9.8351	9.6314	0.2040	0.0003	0.1	99.9

II. CATALYTIC UPGRADING IN CLATHRATE MEDIUM

1. INTRODUCTION

It is clear from data presented in earlier sections of this Report that the clathrate/solvent medium is capable of mobilizing coal with approximately the same efficiency as pyridine (*i.e., ca* 23% dissolution, compared with 4% in benzene, 0.1% in cyclohexane under comparable conditions) although the material extracted may not be the same in each case. The action of the clathrate phase upon the coal is a physical process the nature of which is not yet understood and remains a complex problem which is inextricably bound to the yet indeterminate general structure of coal. The advantage of the clathrate treatment over pyridine extraction lies not in the area of % dissolved yield, however, but in the potential of the clathrate for supporting and retaining an upgrading catalyst for hydrogenation under mild conditions of temperature and pressure. Successful further development of the clathrate concept as a low-severity regime for coal dissolution and upgrading which ultimately will afford acceptable conversion yield to liquid hydrocarbons rests on identification of conditions in which the clathrate behaves as a medium for catalytic hydrogenation at the same time immobilizing catalyst components in a stable homogeneous phase. This is a complex experimental problem because the general solvent properties of the clathrate systems are yet poorly understood, but a start has been made during Phases I and II of this project (1983-84) and a systematic programme of investigation has been proposed as Phase III.

Identification of a suitable clathrate-soluble hydrogenation catalyst would open up the possibility of upgrading of clathrate-soluble coal-derived material with consequent phase-transfer from clathrate into the solvent phase. It should be noted that a homogeneous catalyst will be required for this application: conventional heterogeneous upgrading catalysts are not designed to work at low temperatures and would be susceptible to physical poisoning under the conditions employed. Since little information is available concerning solvation or solvolysis effects in the clathrate phase, identification of a solute which will act as a homogeneous hydrogenation catalyst in such an unusual chemical environment is a non-trivial problem. Accordingly as a starting point we have concentrated our attention around the previous claims of the Alabama group; we have also recently begun to examine the stability of several established molecular transition-metal catalysts in the clathrate in relation to effectiveness for hydrogenation of model unsaturated organics.

There is accumulating evidence that non-protic strong acidic substances (in particular BF_3 or the aluminum halides) can induce hydrogenation and rearrangement of polycyclic hydrocarbons. Recent examples of this include high-temperature dismutation of hydroaromatics such as tetralin, hydrogenation of a variety of polyaromatics, alkylation of benzene, and most currently from work in this laboratory low-dilution, ambient conversion promoted by $AlCl_3$ of naphthalene to reduced and structurally modified hydrocarbons. Chemical relationships between aluminum halides and the aluminum alkyls which constitute an essential ingredient of the Group III class of clathrates led Atwood's group to examine the effect on representative clathrates of addition of AlX_3 (X = Cl, Br, I). Adapting this idea to a different context the effect of $AlCl_3$ addition to the clathrate in coal extraction has recently been examined as an element of Phase II: significant stabilization of the clathrate at elevated temperatures has been observed and improved extraction efficiency and product distribution is evident.

The unique physical properties of the clathrate phase impose stringent constraints on the type of catalytic substrate which may be introduced without the prospect of continual loss via leaching into the solvent part of the biphase system. The chemical properties of the clathrate phase in terms of generalized solvent behaviour remain largely unknown. With such uncertainties directions to be followed are necessarily to some extent intuitive, but a similar strategy is common to the whole field of catalysis: progress is built on examining parallels with existing successful procedures. Preliminary experiments conducted as a part of Phase II, discussed in detail below, have yield important information which will be helpful in defining a logical approach.

Identification of a hydrogenation catalyst comparible with the clathrate medium and suitable for in situ upgrading of solubilized coal-derived material is subject to several severe constraints incuding the following:

(i) Catalyst activity must be maintained at temperatures not exceeding 180°C and activity at ambient would be an advantage. The catalyst must ideally also be effective at low hydrogen pressures.

(ii) The catalyst must be soluble in and be unaffected by the clathrate or be alkylated by it to a species possessing comparable (or superior) activity. The active species must be stable over long periods in the clathrate phase.

(iii) Ideally the catalyst should be immobile in the clathrate phase, *i.e.* transfer to the solvent phase should be prevented by solubility characteristics of the active species.

These considerations immediately rule out a range of well-established homogeneous transition-metal catalysts so that our approach has been to assess the early reports from the Alabama group while at the same time setting up a systematic examination of the problem.

2. PROGRESS DURING PHASE II

It has been suggested on the basis of trial experiments conducted during 1982-83 at the University of Alabama that certain organometallic complexes enhance coal-extraction by liquid clathrates. We have tested the effect of the following compounds upon yields of soluble material obtained from Devco and K-seam coals: $(\eta^5\text{-}C_5H_5)Mn(CO_3)$, $(\eta^5\text{-}MeC_5H_4)Mn(CO)_3$, $Fe(\eta^5\text{-}C_5H_5)_2$, $(\eta^6\text{-mestiylene})Cr(CO)_3$. In all cases runs were conducted at 70°C for 4 hr under 1 atm of H_2, with 2 g additive, 10 g coal, and 100 ml each of liquid clathrate and toluene. No measurable effect upon yield or composition of soluble coal-derived material was observed for any of these additives, although contamination of the toluene phase above the liquid clathrate with transition-metal complex or derived material made exact yield-determinations difficult as illustrated in Table 8.0. However in view of improved analytical methodology for determination of product yields and in the light of our more recent experiments at 500 psi H_2 gas, 120-180°C this approach might be worth re-evaluating.

Table 8.0. $(C_5H_5Mn(CO)_3)$ as Clathrate Additive in Experiments with Devco Coal

Reaction	Toluene Solubles	$CHCl_3$ Solubles		Pyridine Solubles		Insolubles		Total		Overall Total
		Clathrate	Coal	Clathrate	Coal	Clathrate	Coal	Solubles	Insolubles	
#10-23	0.830g	0.564	0.281	0.206	0.587	0.110	9.255	2.468	9.365	11.833
#10-24	0.921g	0.466	0.261	0.150	0.985	0.047	8.577	2.783	8.624	11.407
Mn conc.	16.3%	10.2%	2.31%	155ppm	36ppm	139ppm	26ppm			
Mn correction	-.558g	-.176	-.022	-	-	-	-	-.756	-	
Corrected yields	0.363	0.290	0.239	0.150	0.985	0.047	8.577	2.027	8.6	651

Mn in Devco coal is 152ppm.

Since aluminum alkyl clathrate formation depends on interaction between AlR_3 and an ionic component, it seemed to us to be a logical further step to examine incorporation of salts derived from the Mn, Fe, or Cr transition-metal additives as integral clathrate components in novel clathrate phases. In accord with such expectations, representative reactions in toluene between cationic Mn and Fe species and $AlEt_3$ leads to facile formation of two-phase liquid systems based on $[Fe(\eta^5-C_5H_5)(arene)]^+$ or $[Mn(CO)_3(\eta^6-arene)]^+$ which are able to sustain liquid clathrate behaviour (as PF_6^- salts, with $AlEt_3$/toluene, Table 9.0).

Table 9.0. Transition Metal Cation-based Liquid Clathrates.[a]

Cation[b]	Colour	A/A[c]	Stability
$[FeCp(mesitylene)]^{+d}$	brown	20 ± 1	e
$[FeCp(tetralin)]^{+d}$	brown	30 ± 2	e
$[Mn(CO)_3(mesitylene)]^+$	yellow	29 ± 4	f
$[Mn(CO)_3(tetralin)]^+$	orange	30 ± 4	e

[a] Using toluene as aromatic medium.

[b] PF_6^- is the counter ion.

[c] Based upon average ratio of toluene to cation integrations (^1H 90 MHz spectra).

[d] Cp = $C_5H_5^-$.

[e] Remains stable for several weeks under ambient conditions but discolouration to toluene phase does occur.

[f] Relatively rapid discolouration (< 1 day) to blackish green colour occurs within one day.

Synthetic details are included in Appendix II. These new systems are stable for months under ambient conditions, although in a minor side-reaction alkylated, neutral metal compounds (one of which has been identified as a hexadienyl derivative resembling the neutral organometallic additives described above) form slowly and are leached into the solvent phase under trial extraction conditions. It has been subsequently shown, however, that incorporation of these novel liquid clathrates (arene = tetralin, mesitylene) in extraction experiments conducted under ambient pressure of hydrogen gas likewise results in no increase in coal liquid yield, although quantification was once again complicated because of the presence of additive-derived materials in the solvent phase. On the basis of these experiments we are of the opinion that some of the earlier conclusions arrived at by the Alabama group may have been in error due to inadequate analytical routines for workup.

To evaluate the effect of an anionic component with well-established activity in homogeneous hydrogenation the iron complex $[HFe(CO)_4]^-$ was also investigated as a potential clathrate constituent. Synthetic details for isolation of appropriate tetra-alkylammonium salts are included in Appendix II. In this case, treatment of the transition metal species with $AlEt_3$ in excess toluene led only to reaction to give unidentified products and there was no evidence for formation of a layered (clathrate) liquid system.

As an alternate parallel approach, preliminary experiments to test the effect of dispersion of a conventional homogeneous hydogenation catalyst in the (aluminum alkyl/tetraalkyl ammonium halide) clathrate system were conducted, beginning with the cobalt complex

$Co[P(OMe)_3]_3(\eta^3-C_3H_5)$, 1, which was first reported by Muetterties and coworkers and has subsequently been shown to hydrogenate arenes and polycyclic aromatics at room temperature in non-polar solvents. Although it has been suggested that 1 is not suitable for coal liquefaction this was under experimental conditions that do not resemble those operating in a liquid clathrate extraction. For this reason 1 was chosen as a possible candidate for clathrate compatibility; however after isolation in the manner described in Appendix II it was found to decompose rapidly on contact with liquid clathrate to give a reaction mixture which was not active in hydrogenation.

The ruthenium(II) complex $RuCl_2[P(C_6H_5)_3]_3$, 2, and its hydrido-derivatives are well established as catalysts in a number of roles, including hydrogenation of alkenes and hydrogen-transfer reactions. It has also been demonstrated previously that 2 remains active in the presence of Lewis acids including $AlMe_3$, so that decomposition was not anticipated in the liquid clathrate medium. Synthetic details for complex 2 are included in Appendix II. A series of experiments was conducted at 1 atm. H_2 gas, ambient temperature, to assess the effectiveness of compound 2 dispersed in the clathrate medium for hydrogenation by using 1-octene as a model substrate. Data are collected in Table 10.0. These results confirm conclusively that hydrogenation of 1-octene occurs at a qualitatively similar rate to that observed in a more conventional solvent medium, although further work is required to test the generality in relation to internal olefins and hydrogenolysis activity. No reduction of phenanthrene was observed (Table 10.0), indicating that 2 is not likely to effect aromatic

Table 10.0. Catalytic hydrogenation ability of $RuCl_2(PPH_3)_3$ in liquid clathrate media[a]

Substrate	Quantity	Catalyst wt. (mg)	Ratio	Reaction[b]	Time	%hydrogenated[c]	%isomerized[c,d]	%unchanged[c]
1-octene	2 ml	100	123	Toluene 15 ml	20 hr	66	0	34
1-octene	0.5 ml	25	123	Toluene 15 ml	20 hr	100	0	0
1-octene	3 ml	0	-	-	20 hr	0	0	100
1-octene	3 ml	150	123	-	20 hr	60	28	12
1-octene	0.5 ml	25	123	-	4 hr	44	15	41
1-octene	0.5 ml	25	123	-	20 hr	75	19	6
Phenanthrene	0.5 g	25 mg	108	-	20 hr	0	0	10
1-octene	0.5 ml	25 mg	123	l.c., 15 ml no toluene	20 hr	97	3	0

[a] all reactions conducted under ambient conditions

[b] 15 ml $[NPr_4][Al_2Et_6I]$ nxylene liquid clathrate and 15 ml toluene unless otherwise noted

[c] as determined by G.C. integration

[d] identified as isomers of 1-octene via G.C./M.S.

hydrogenation; but some evidence was obtained for isomerization of 1-octene to other isomers (Table 10.0), a novel result which again requires further investigation.

Following the demonstration that complex 2 can in principle behave as a hydrogenation catalyst in the aluminum alkyl phase the same compound was introduced on a catalytic scale in extraction experiments using initially 1 atm. pressure of H_2 gas at 120°C and subsequently 500 psi (ca 35 atm.) H_2 gas in a pressure-reactor at 120 then 180°C. The results are set out in Table 11.0, together with data from control reactions in the absence of added H_2 at 100, 120, and 140°C (Runs 10.48, 10.64, and 10.63 respectively). It should be noted that these latter profiles provide evidence for a noticeable increase in yield of solubles with increasing temperature (although the mass balance in experiment 10.64 is poor). The apparent inconsistency of runs 10.60 and 10.67 arises because in the former material accumulated in the insoluble fraction recovered from the clathrate phase at the expense of pyridine solubles in Residue (B), behaviour which we have noted elsewhere. The overall conclusion at this stage, based on comparing the yields under both low and intermediate H_2 pressures, was that significant further mobilization of the coal mass accompanied the addition of catalytic amounts of the Ru complex increasing the total solubles to >20% (maximum 28% in run 10.73).

The rhodium(I) complex $RhCl(PPh_3)_3$, 3 ('Wilkinson's catalyst') is perhaps the most powerful homogeneous hydrogenation catalyst system yet discovered and is effective in alcoholic solution at ambient temperature and H_2 pressure. The increase in overall yield and

Table 11.0. Comparison of $RuCl_2P_4$ (100 mg/run) and Control Experiments in Xylenes.

	Temp./Condns.	Tetralin/ Xylene Layer	Clathrate Layer (C)			Residue (B)			Total Sol.	Total Insol.
			Chloro. Sol.	Pyr. Sol.	Insol.	Chloro. Sol.	Pyr. Sol.	Insol.		
Controls										
10-48	100/no H_2	0.143	0.183	0.393	0.117	0.009	0.528	7.550	1.256	7.667
10-64	120/no H_2	0.170	0.182	0.581	0.176	0.170	0.234	9.042	1.337	9.218
10-63	140/noH_2	0.184	0.235	0.696	0.400	0.129	0.602	6.959	1.846	7.359
Catalyst										
10-60	120/1 atm. H_2	0.117	0.207	0.476	1.408	0.143	0.554	7.247	1.497	8.655
10-67	120/1 atm. H_2	0.184	0.214	0.723	0.678	0.180	1.070	6.613	2.371	7.291
10-74	120/500 psi H_2	0.213	0.213	0.883	0.241	0.101	0.641	6.823	2.051	7.063
10-72	180/500 psi H_2	0.352	0.109	1.201	0.309	0.212	0.357	6.771	2.231	7.080
10-73	180/500 psi H_2	0.267	0.181	0.817	0.118	0.183	1.333	6.388	2.781	6.506

Table 12.0. Comparison of $RhClP_3$ and Control Experiments

Pressure: 500 psi hydrogen
Solvent: mixed xylenes
Temperature: 120°C

	Conditions	Tetralin/ Xylene Layer	Clathrate Layer (C)			Residue (B)			Total Sol.	Total Insol.
			Chloro. Sol.	Pyr. Sol.	Insol.	Chloro. Sol.	Pyr. Sol.	Insol.		
Controls										
10-75	7.5g coal, 500 psi H_2, No catalyst, No $AlCl_3$	0.110	0.166	0.630	0.205	0.084	0.505	5.493	1.495	5.698
10-79	7.5g coal, 500 psi H_2, No catalyst, No $AlCl_3$	0.148	0.125	0.602	0.201	0.066	0.628	5.356	1.569	5.556
$RhClP_3$ Catalyst										
10-76	7.5g coal, 500 psi H_2, 100 mg $RhClP_3$, No $AlCl_3$	0.206	0.194	0.689	0.210	0.194	0.567	5.205	1.758	5.415
10-78	7.5g coal, 500 psi H_2, 100 mg $RhClP_3$, No $AlCl_3$	0.149	0.158	0.721	0.221	0.087	0.465	5.522	1.580	5.743

120° **No catalyst present** - Average combined weight of solubles = 0.976g = 13.99%
(ex cold pyridine coal residue extraction) daf
Total soluble 21.96%

120° **Catalyst present** - Average combined weight of solubles = 1.153g = 16.53%
(ex cold pyridine (B) coal residue extraction)
Total soluble 23.93%

140° **Catalyst present** - Combined weight of solubles = 1.294g
(ex cold pyridine coal residue extraction) 18.55%
- **Total soluble** 2.040g
(incl. cold pyridine extraction of residue) 29.25%
- **Total soluble** 2.439g
(incl. **ash-free** pyridine insoluble material in clathrate phase) 34.97%

changes in solvent distribution of mobilized mataerial associated with introduction of the Ru complex led us to examine the action of compound 3, (the synthesis of which is described in Appendix II), again in catalytic proportion *vs*. clathrate as medium and coal as substrate and using 500 psi of H_2 gas. Data from representative extraction experiments (runs 10-76, 10-78) are summarized in Table 12.0. As indicated at the base of the Table, a marked increase in overall yield was again evident (to a maximum of 35% at 140°C) with a shift to concentrate the mobilized material in the more soluble fractions. In the presence of added H_2 the Ru and Rh species thus showed a similar influence to one another on the coal dissolution phenomenon, in a manner consistent with the established catalytic performance of each.

As part of the programme of extraction runs conducted under H_2 gas a series of control experiments was also included. Comparison of the results using 500 psi H_2 at elevated temperature with corresponding data obtained when either Ru or Rh species were used exposed a surprising and extremely significant detail, which is illustrated in Table 13.0 using figures from runs 10-74, 10-76, 10-79, and 10-80 - 10-82. It is apparent that a substantial improvement in liquefaction characteristics accompany exposure of the extraction medium to only *moderate* pressures of H_2 *in the absence of catalyst* and at temperatures *well below* those demanded by current hydroliquefaction approaches. There is a trend towards increasing yields in most operations in the workup procedure as Ru or Rh catalyst is introduced (see 10-79/10-74/10-76) but the effect is not so marked as was suggested from the isolated catalytic runs. Comparison of the results for

Table 13.0. Effect of Temperature and Catalyst at 500 psi H_2 Gas.

Temp./Condns.		Tetralin/ Xylene Layer	Clathrate Layer (C)			Residue (B)			Total Sol.	Total Insol.
			Chloro. Sol.	Pyr. Sol.	Insol.	Chloro. Sol.	Pyr. Sol.	Insol.		
120°C/500 psi H_2										
10-79	No catalyst	0.148	0.125	0.602	0.201	0.066	0.628	5.356	1.569	5.556
10-74	Ru catalyst	0.160	0.160	0.664	0.181	0.076	0.482	5.130	1.542	5.311
10-76	Rh catalyst	0.206	0.194	0.689	0.210	0.194	0.567	5.205	1.758	5.415
140°C/500 psi H_2										
10-82	No catalyst	0.138	0.159	0.910	0.440	0.092	0.737	4.846	2.036	5.286
10-80	Rh catalyst	0.131	0.168	0.869	0.399	0.126	0.746	5.281	2.040	5.680
10-81	No catalyst/80 psi Ar	0.114	0.132	0.675	0.176	0.088	0.653	5.188	1.652	5.364

runs 10-82 (140°C, 500 pasi H_2, no catalyst) and 10-81 (140°C, 80 psi Ar, no catalyst) is even more remarkable and emphasizes the effect of H_2 pressure on the dissolution efficiency: conspicuous decreases are evident in yields from all stages of the workup when the hydrogen overpressure is replaced by an inert gas (argon). Viewed together, the results collected in Tables 11.0 - 13.0 suggest autocatalytic behaviour of the coal/clathrate mixture at elevated temperature under H_2 gas, at least for Devco coal. This observation may prove to be exceptionally important for any future studies, especially since it is supported in part by a similar though qualitative effect tentatively attributed to the same coal during Phase I experiments.

To address the usefulness of Lewis acids as additives in the clathrate extraction process, representative compounds including $AlCl_3$, $SnCl_4$, $TiCl_4$, and $ZnCl_2$ were investigated. Anhydrous zinc chloride proved to be insoluble in the clathrate and was unaffected by it but each of the other chlorides dissolved in the bilayer system with no apparent change in character: in particular no deterioration was noted in any instance on heating at 120°C for 20 hr. Experimental data obtained using 1 atm. H_2 pressure at 120°C are summarized in Table 14.0. Yields of solubles are increased to a broadly similar extent in the presence of each additive. With $SnCl_4$ (run 10-62) and even more markedly with $TiCl_4$ (run 10-61), however, much greater mobilization from the coal into the clathrate phase is indicated by the large fractions of chloroform/pyridine insolubles accumulated in the clathrate layer (C), material which contained <2% ash and is clearly coal-derived. Accordingly the clathrate phase was in in each case distinctly more

Table 14.0. Effect of Lewis Acid Additive, 120°C/Xylenes/1 at H_2.

Expt. No.	Temp./Condns.	Tetralin/ Xylene Layer	Clathrate Layer (C)			Residue (B)			Total Sol.	Total Insol.
			Chloro. Sol.	Pyr. Sol.	Insol.	Chloro. Sol.	Pyr. Sol.	Insol.		
10-64	No H_2	0.170	0.182	0.581	0.176	0.170	0.234	9.042	1.337	9.218
10-66	$AlCl_3$ (2 g)	0.213	0.152	0.472	0.192	0.109	0.790	7.092	1.737	7.284
10-62	$SnCl_4$, (0.3 ml)	0.200	0.144	0.638	0.697	0.121	0.489	7.405	1.592	8.102
10-61	$TiCl_4$, (0.2 ml)	0.199	0.194	0.603	1.097	0.111	0.433	6.324	1.540	7.421

viscous in appearance in the final stages of extraction than in any comparable experiment not involving MCl_4 (M = Sn or Ti), suggesting a different mode of action on the coal-mass than encountered hitherto. These indicators though of a preliminary nature provide impetus for further work in this area.

A further important effect on the clathrate accompanying addition of $AlCl_3$ was distinguished and has been confirmed independently in a different context by the Alabama group. Trial extraction runs using the $AlEt_3$-based clathrate carried out under hydrogen pressure at 180 °C (rather than 100-140°) led to complete degradation of the two-phase system. However addition of $AlCl_3$ (up to 50 mol % without change in clathrate appearance) afforded a system which was stable to such decomposition, permitting comparative experiments to be conducted at the higher temperature as discussed elsewhere. This stabilization has tentitively been attributed to formation of mixed alkyl(chloro)aluminum species in the clathrate which are more stable to hydrolytic cleavage reactions by water or other sources of OH or O, and should be viewed as a parallel with the successful development of air-stable liquid clathrate analogues by Atwood and co-workers.

3. INTERIM CONCLUSIONS

Because of the complexity of the product mixtures obtained as solubilized material during the extraction procedure, evaluation of the success of attempts at in situ upgrading relies heavily in the first instance on monitoring increases in overall extraction efficiency on a comparative basis. Such effects have been rendered accessible only by careful development of a work-up and analytical routine which gives consistently reliable mass-balances. Achievement of this goal has led to a situation in which it is possible to use residual coal-mass as a further accurate measure of degree of dissolution as reflected in the data of Tables 11.0-14.0. The results of a preliminary examination of effects which may promote liquid clathrate extraction of coal, including addition of species which may act as upgrading catalysts, may tentatively be interpreted as follows:

1. Increasing dissolution accompanies increasing temperature in the range 100-140°C;

2. Moderate pressures of added hydrogen gas (typically 500 psi) leads to enhanced coal mobilization;

3. Addition of organometallic additives e.g. $Fe(C_5H_5)_2$ or $Mn(C_6H_6)(CO)_3$ or use of clathrates based on derived organometallic cations at ambient hydrogen pressure appears to result in changes which are only marginal;

4. Addition of conventional hydrogenation (Rh) or hydrogenolysis (Ru) catalysts as trace additives leads to a modest increase in dissolution yields at ambient hydrogen pressure or at 500 psi;

5. Addition of sub-stoichiometric amounts of Lewis acids such as $TiCl_4$ has a beneficial influence on extraction characteristics which warrents further investigation;

6. Use of moderate pressures of added hydrogen at moderate temperatures markedly improves yields of dissolved material in a manner which suggests autocatalysis by agents in the coal-mass and which

warrants further attention;

7. Addition of up to 50 mol% $AlCl_3$ to the $AlEt_3$-based liquid clathrates results in dramatic stabilization at elevated temperature which may be related to factors which are important in the design of air-stable liquid clathrates.

III. COAL STRUCTURE: THE NATURE OF THE DISSOLVED MATERIAL

1. INTRODUCTION

The high molecular weight constituents of coal are much more difficult to define (than volatile components) insofar as they (1) cannot be extracted by solvent and (2) cannot be "distilled from the coal without thermal decomposition to low molecular weight fragments". This quote from the recent text on coal structure by Speight[1] summarizes the rationale for examining the coal macromolecules in the clathrate phase. As a new solvent, one might project that additional different (and unaltered) structures could be solubilized relative to classic solvents. A number of techniques have been applied to the preasphaltene-like material in the clathrate phase and in several instances properties have compared with pyridine reflux derived material.

Most data to date, as the following sections reveal has shown few definite differences between the two solvent systems. Higher current yields at 140-180°C including substantial non-centrifugeable pyridine insoluble material in the clathrate phase indicate that further pursuit of macromolecular structure via liquid clathrate systems should be undertaken.

---

[1] Speight, J. G. "The Chemistry and Technology of Coal", Chemical Industries Series, Marcel Dekker, New York, 1983.

2. APPLICATION OF ARSENIC TRICHLORIDE AS AN NMR SOLVENT FOR HIGH MOLECULAR WEIGHT COAL-DERIVED MATERIALS

(i) Background

The choice of a solvent for coal derived materials has posed a problem for many workers, especially in attempts to investigate the higher molecular weight asphaltenes or other relatively insoluble fractions by using one or more spectroscopic techniques. This problem is especially serious when characterizing the pyridine soluble (preasphaltene) liquefaction products of coal. Solvents that have been used, such as $CDCl_3$, CS_2, CCl_4, toluene, hexane, and tetrahydrofuran all suffer from the drawback that they are not able to dissolve all of the pyridine soluble fraction. As a consequence the spectra recorded of coal derived material dissolved in these solvents do not represent the entire range of molecular structures in the pyridine soluble fraction. d-5-Pyridine is itself unsuitable to use as a solvent since the aromatic nature of the pyridine molecule results in interferences in IR and NMR spectra of the highly aromatic coal-derived material being investigated. The NMR spectra recorded of solid state samples, while avoiding some of the problems discussed above, suffer from a lack of resolution (1).

In this contract year, we have developed the use of $AsCl_3$ as a solvent for coal-derived materials including the pyridine soluble fraction from the clathrate layer which avoids the problems of interfering resonance signals discussed above. The use of $AsCl_3$ as a solvent also permits the measurement of ^{13}C NMR spectra of the high molecular weight fractions in solution rather than by the less satisfactory solid state technique. The use of $AsCl_3$ as a proton NMR solvent was reported by Szymanski et al some time ago in their studies of phenolic resin polymers (2, 3). Bose et al reported its use as a solvent for ^{13}C NMR studies some time later (4).

The study of pyridine extracted coal material is complicated by the difficulty of removing the last traces of pyridine from the dissolved product. Reports of up to 20% by weight of the final product being retained pyridine, even after pumping at low vacuum for 20 hours or longer have been confirmed in this laboratory, as detailed in Results, Section I. In addition, our observation is that this pyridine contaminated coal residue is hygroscopic. Other workers have reported the removal of pyridine using supercritical gas extraction with CO_2 (6), or washing with dilute HCl (7, 8) or with repeated methanol washes followed by vacuum drying steps (9). The precipitation of the pyridine-soluble fraction from solution in the pyridine as reported by Erbatur et al (7) suffers from the retention of pyridinium hydrochloride, a difficulty repeatedly experienced in our laboratory, even after extensive washing.

Experimentally, use of $AsCl_3$ has been straightforward, see Appendix II-3 for detail. However, significant precautions should be taken.

In using this material, it is mandatory to perform all transfers in the fumehood, and to wear protective glasses. The hazardous nature of the material should be recognized. Sample tubes are sealed (paraffin or polythene film) to protect against absorption of moisture by hygroscopic $AsCl_3$. Samples prepared in this fashion show no deterioration (spectra changes) over 48 hours, though spectra are normally recorded immediately.

(ii) Application of $AsCl_3$ in Obtaining ^1H and ^{13}C Spectru

A typical 250 MHz proton NMR spectrum of the pyridine-soluble component of the clathrate phase from Devco and recorded in d5-pyridine is shown in Figure 3.0, Experiment 10-29, see Table 15.0. In contrast, the spectrum in $AsCl_3$, Figure 4.0 shows a complete absence of interfering resonance in the aromatic region. Similarly interference-free C^{13} spectra can be obtained, Figure 5.0; now of a K-seam clathration experiment, 2-47, see Table 15.0. Note the deliberate use of $CDCl_3$ as an internal reference (77.0 ppm).

(iii) Analysis of Spectra

The proton magnetic resonance data have been used by many workers to yield information on the molecular structure of the coal-derived material (1, 10-12). One of the parameters of significant interest is the fraction of carbon atoms which are aromatic (designated f_a). Indirect estimations of f_a have been made using the Brown-Ladner equations. The equations that are employed are provided in Appendix III-2. More recently, C^{13} NMR spectra of solid samples have been successfully used to derive f_a directly. The values obtained by the two methods have been shown by Retcofsky to be in agreement (12). Similarly, a comparison between f_a values obtained using Brown-Ladner equations, modified Brown-Ladner equations and those obtained from C^{13} NMR spectra of $AsCl_3$ solutions of pyridine soluble

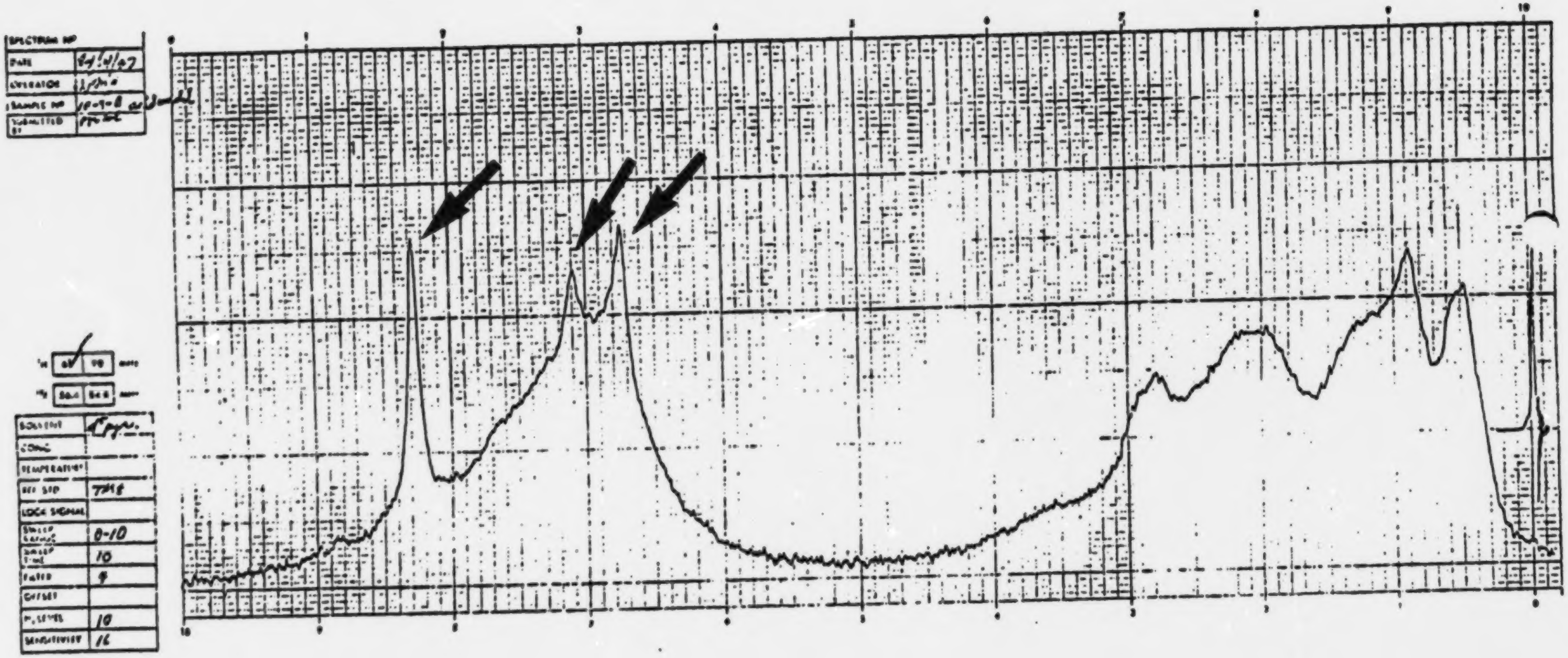
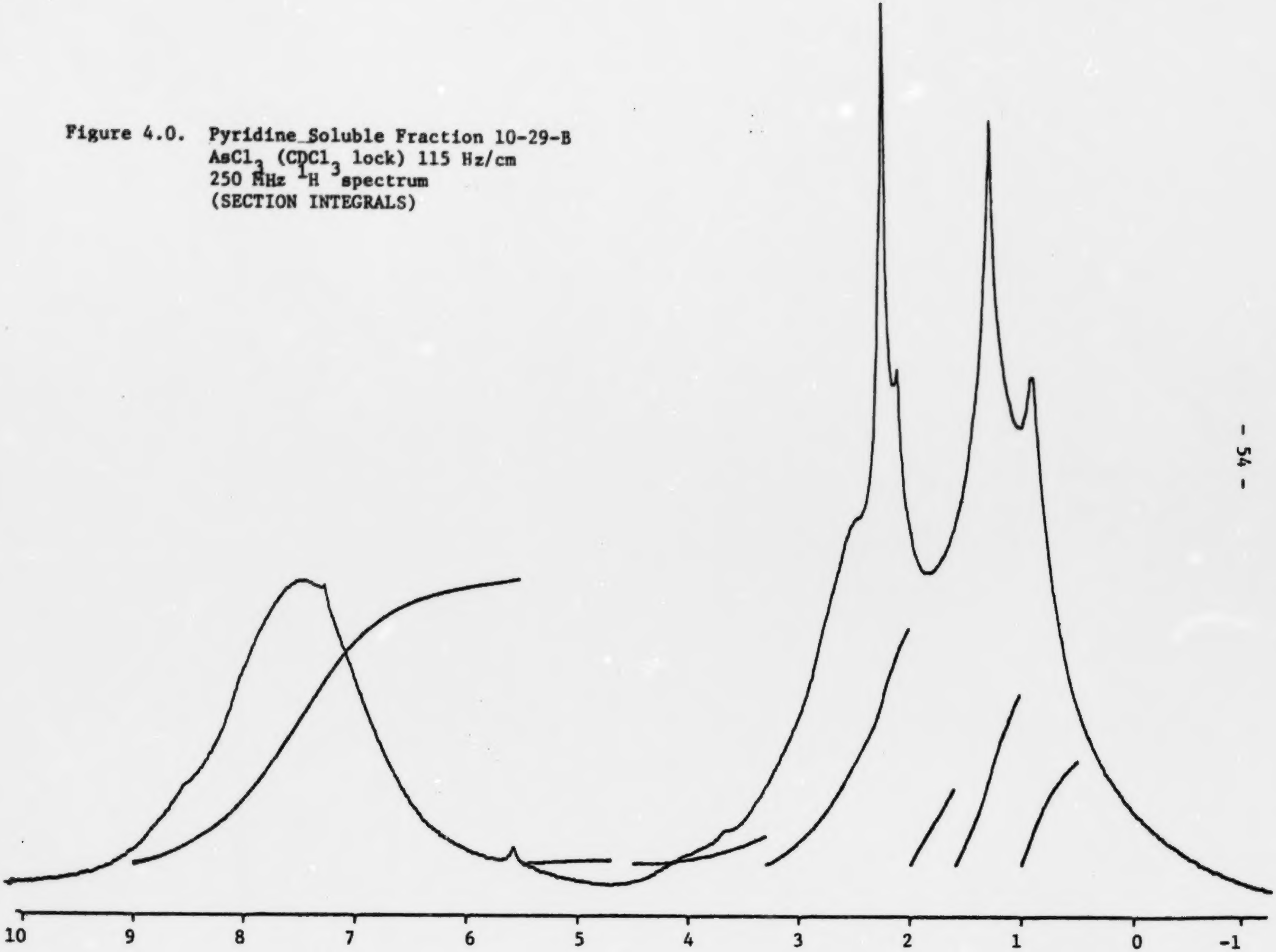


Figure 3.0. ^{1}Hmr Pyridine Soluble Fraction 10-9-B (Acid washed) d-5 Pyridine 60 Mhz/TMS
NOTE RESIDUAL PYRIDINE RESONANCES →

Figure 4.0. Pyridine Soluble Fraction 10-29-B
$AsCl_3$ ($CDCl_3$ lock) 115 Hz/cm
250 MHz ^1H spectrum
(SECTION INTEGRALS)



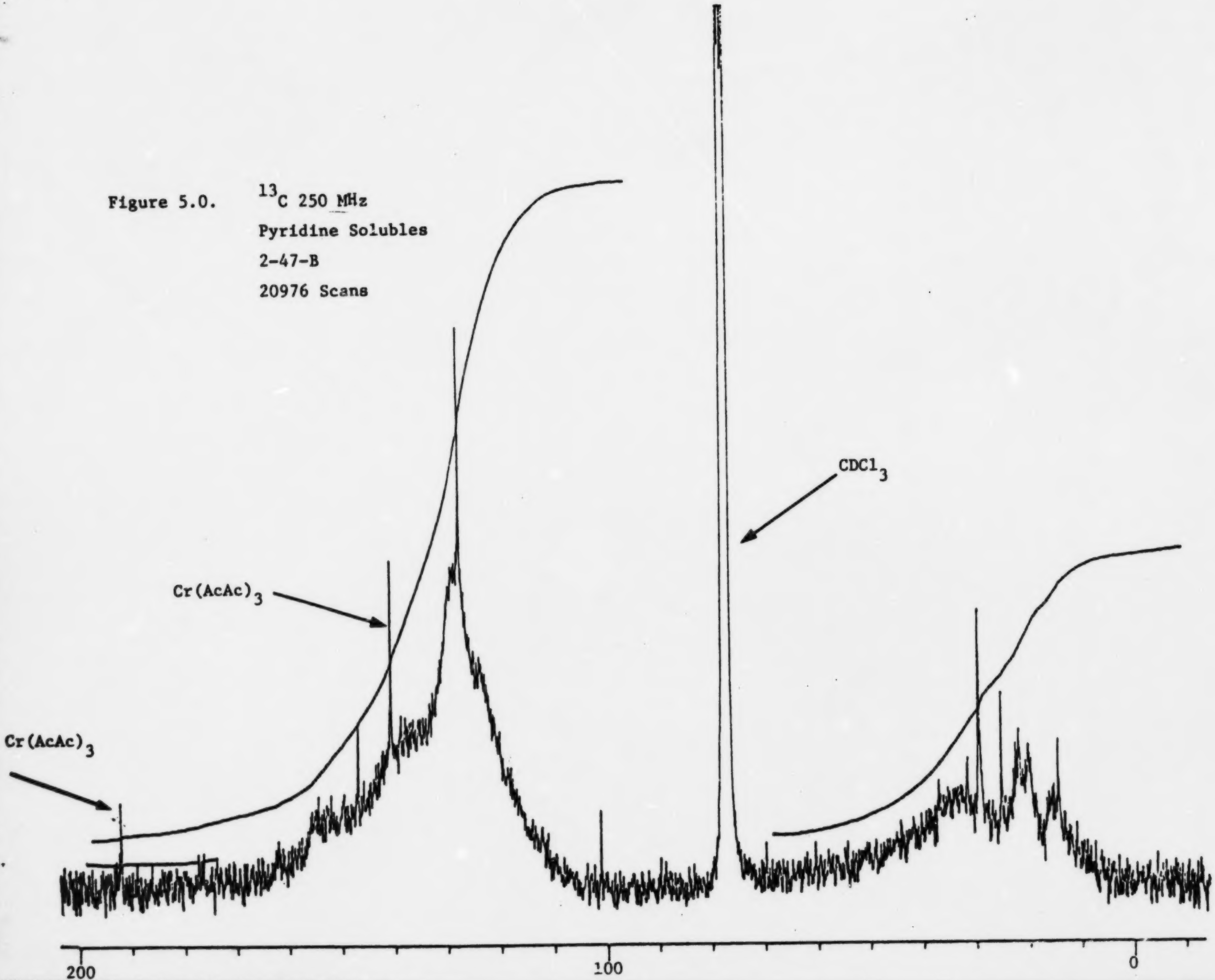


Figure 5.0. ^{13}C 250 MHz
Pyridine Solubles
2-47-B
20976 Scans

preasphaltenes show differences of the same order as those quoted by Retcofsky (see Table 15.0). It is noted that both serial samples from K-seam, Cretacous coal and from Devco (of ≈ same rank but Carboniferous) show consistent f_a values close to 0.76 for the Yen modification (14). These values are in remarkably good agreement with the f_a values determined directly from C^{13} nmr spectra recorded on pyridine soluble material dissolved in $AsCl_3$. Both sets of values are somewhat different from those calculated using Bartle's application of the Brown-Ladner equations however.

Other molecular parameters derived from the equations are also shown in Table 15.0. It can be seen that there are few significant differences between results for the replicate samples of the same coal or even between the two different coals. Recall that K-seam is a high volatile, bituminous A, low sulphur sample with a Ro (mean maximum reflectance) value of 0.85. The Devco coal is also high volatile but has high sulphur content (1.69%) typical of eastern coals.

In addition to the extended analysis reported in Table 15.0, we also carried out simple comparison of the fraction of carbon atoms and of the protons that are aromatic, (f_a^* and $f_a^{\neq}$ values). Representative data is shown in Table 16.0 and in many cases refers directly to the same samples as Table 15.0. Again we note that the variation from run to run encompasses the differences in the observed ratios; with

Table 15.0. Modified Brown Ladner Analysis of NMR Spectra of Pyridine Soluble Material from K-seam and Devco Coals

	f_a			H_{aru}/C_{ar}		σ		η
Coal Sample	Bartle	Yen	f_a^*	Bartle	Yen	Bartle	Yen	Yen
2-47-B (K/Clathrate)	0.84	0.73	0.74	0.57	0.60	0.43	0.53	1.93
11-2-9 (K/Reflux Pyridine	0.84	0.76	0.71	0.55	0.57	0.41	0.51	2.32
11-2-11 (K/Reflux Pyridine)	0.84	0.75	0.75	0.58	0.57	0.41	0.52	2.20
10-29-B (Devco/ Clathrate)	0.83	0.76	0.74	0.49	0.53	0.14	0.60	1.97
11-10-12 (Devco/ Reflux)	0.86	0.76	0.78	0.57	0.64	0.31	0.37	2.59

Definitions: f_a = fraction of total carbon which is aromatic carbon

H_{aru}/C_{ar} = ratio of substitutable aromatic edge atoms to total aromatic atoms

σ = fraction of available aromatic edge atoms occupied by substituents

f_a^* = fraction of total carbon which is aromatic, ^{13}Cmr

η = number of carbon atoms in average alkyl substituent

Table 16.0. ^1H and ^{13}C NMR Data

Reaction	No.	Treatment	f_a[*]	f_a[‡]
K-seam	11-2-9	pyridine reflux	.72	.36
K-seam	11-2-11	pyridine reflux	.77	.42
K-seam	2-47-B	clathration	.69	.36
Devco	11-10-9	pyridine reflux	.74	.30
Devco	10-29-C	clathration	.71	.29
Mary Lee	11-14-2	reflux	.76	.40

[*] Fraction of carbon atoms which are aromatic.

[‡] Fraction of protons which are aromatic.

the possible exception of the low aromatic proton values for the Devco coal (0.30 and 0.29). On the basis of current data we conclude that clathration and reflux are isolating material of the same degree of aromaticity and aromatic hydrogen ratio.

The availability of $AsCl_3$ as a solvent for pyridine soluble preasphaltene coal material will simplify C^{13} nmr work for these fractions very significantly. The higher resolution obtained from solution nmr vs solid state nmr will facilitate the assignment of C^{13} nmr signals of the higher molecular weight preasphaltene material in a manner similar to that reported in the survey by Snape et al (16). In addition, information such as the mean degree of aromatic condensation is expected to be more easily derived from the better resolved solution spectra of solid state samples where peak overlap problems such as those described by Burgar have to be overcome (17).

It has been found that it is particularly important to achieve the highest NMR solvent polarity possible for pyridine extracted material.

For example, such coal extracts have been found to contain typically only 20% to 70% tetrahydrofuran soluble material (the lower ranges are obtained after short air exposure of the extracts). This is in contrast to the typically complete initial solubility in tetrahydrofuran of high temperature hydroliquefaction residues. Such an observation is consistent with retention of more polar functional groups in the refluxing solvent or liquid clathrate derived product (low severity conditions). References for this section are contained in Appendix III-3.

3. ELEMENTAL ANALYSIS OF COAL FRACTIONS

Close correspondence between the f_a^* and $f_a^{\prime}$ values for *clathrate* and *pyridine* extracts prompted elemental analysis (Carbon and Hydrogen) of a series of preasphaltene fractions, shown in Table 17.0. For continuity in the present comparison, only data from Devco and K-seam coals are shown. One can see that differences between the clathration and refluxing pyridine systems are close to the expectations for the complexity of the work up procedures. In particular for the Devco coal the soluble material *with* asphaltene and oil removed is similar in composition for the two approaches. Coal residues are lower in hydrogen content, but far from depleted. Nitrogen values are disturbingly high relative to analyses of the raw coals (particularly K_B). A more extensive body of analytical data on both reflux and clathrate extraction of a range of coals is contained in Appendix I-4, Table 3. In addition data on the sulphur content of the raw coal, clathrate and residue fractions (Appendix I-4) indicates that the sulphur content of the reflux and clathrate extracted material is similar, and *comparable* for low and high sulphur coals.

Table 17.0. Elemental Analysis.

	Carbon %	Hydrogen %	Nitrogen
Devco Clathrate (10-38)			
Pyridine Soluble	80.19	5.31	2.62
Coal Residue	76.43	5.20	1.77
Devco Pyridine Reflux (11-10-9)			
Pyridine Soluble	82.97	5.97	1.88
Pyridine Soluble Less Toluene Soluble*	81.69	5.27	-
Coal Residue	77.52	4.92	2.11
Devco (Coal)	73.24	4.65	1.57
K-seam			
Pyridine Soluble Clathrate	78.36	5.75	2.07
Reflux**	81.13	5.41	1.81
Residue Clathrate	77.83	4.92	1.77
Reflux	77.73	4.78	1.76
K_B (Coal)	80.90	5.05	0.80

* Contains Chloroform soluble material. In the case of Devco coals we have analysed the toluene-soluble material from the clathrate workup C: 85.20 H: 7.59, indicating the expected higher values.

**Contains chloroform and toluene soluble material.

4. VAPOUR PHASE OSMOMETRY

Since the overall properties of the pyridine soluble fractions clearly allow little discrimination by nmr or elemental analysis, further subdivision of the material has been undertaken.

The first approach adopted was to partition the material on a thermostatted LH20 Sephadex column in dry pyridine, recover the material by precipitation in large volumes of 10% HCl and measure the molecular weight by vapour phase osmometry in dry pyridine relative to benzil and carbowax (MW 1000) standards.

As Table 18.0 shows, for Devco and K-seam the results using this approach showed astonishingly low molecular weights, and a tendency for random failure of the measurement (i.e. fraction 1, Devco). The latter problem may be associated with the extreme sensitivity of these fractions to manipulation (i.e. precipitation and redissolution). Accordingly recently we have begun to measure molecular weight directly on an aliquot from each fraction and back calculate the concentration from the recovery of solid from the remainder of the fraction. As the third column shows, this appears to be a superior procedure, and the experimental details for both the separation and the measurements are reported in Appendix II-4. It should be noted that the sample used (10-64C) was free of any pyridine HCl or other contaminant (for example, xylenes) and we have found "spot" check VPO measurements to be an indicator of incomplete purification. Notwithstanding the relative high values of the initial LH20 fractions, we suspect that underestimation of the molecular weight may still be occurring. In any event, the clathrate soluble material is undoubtedly preasphaltene in character.

Table 18.0. Subdivision of Pyridine Soluble Fractions from Clathrate

K-seam (2-53) (Precipitation)			Devco (10-12) (Precipitation)			Devco (10-64) (Aliquot)		
	Weight %[1]	M.W.[2]		Weight %[3]	M.W.		Weight%[4]	M.W.
V_1	33.5	1338	V_1	26.0	(269)	V_1	11.0	4463
V_2	26.7	1328	V_2	34.3	1453	V_2	21.4	4365
V_3	12.2	662	V_3	10.2	1173	V_3	24.6	4566
V_4	5.4	465	V_4	5.3	*	V_4	16.4	2943
V_5	1.6	*	V_5	3.9	*	V_5	9.0	1933
						V_6	2.5	542
						V_7	2.1	410

[1] 30ml fractions.

[2] Measured in pyridine employing benzil and carbowax standards.

[3] 15ml fractions.

[4] 10ml fractions.

*no measurements made.

5. THERMAL GRAVIMETRIC ANALYSIS

Thermal gravimetric analysis (TGA) offers a means of comparing materials whose low volatility may make them unsuitable for gas chromatographic study. In collaboration with B.C. Research, Vancouver, B.C., we have obtained TGA profiles employing their instrumentation for the toluene soluble material in the clathrate extraction of Devco and K seam coals, Appendix I-3. The striking similarity of temperature dependence in slope and weight percent loss suggest to us again that the inherent molecular distribution in these two coals may be extremely similar reflecting the greater influence of coalifaction (rank) than other geologic parameters.

Examination of the TGA's from the preasphaltene (clathrate soluble) material from Devco clathration experiment and from Devco pyridine reflux again shows that volatility is comparable, though now much less volatilization occurs prior to the 525°C temperature cut off. However the high molecular weight and accompanying lack of volatility is clearly demonstrated by the 65% combustibles observed in the post-ignition phase; Appendix I-3, Figures 3 and 4.

Typical thermograms for Devco and K-seam clathrate soluble material are again shown in Appendix I-3, Figures 6 and 7. Note the low ash content indicating virtually total removal of inorganic contamination from the clathrate. However the large amount of volatile material indicates these latter samples were insufficiently purified prior to examination.

6. VOLATILE COMPONENTS: COMPARISON BY GAS CHROMATOGRAPHY-MASS SPECTROMETRY

Full characterization of coal-derived non-volatiles is extremely difficult, and most explorations of liquefaction processes are forced to focus on the (small) volatile fraction. As detailed in the Report from the first contract year (1983-84) we have separated an oil fraction from the toluene soluble material derived from both pyridine reflux and clathration for K-seam and Devco coals. Oil fractions from toluene reflux extracts for both coals were also obtained. The technique was elution of the toluene soluble material through a simple Silica Sep-pak.

Examination of the data in Appendix I-5 illustrates the approach taken. First as shown in the conventional GC traces I-5-1 and I-5-2 (data shown in Tables 1 and 2 we established that with minor exceptions the state of volatiles obtained for exhaustive pentane extraction of the Sep-pak was extremely similar to the volatile material resulting from use of mixed methylene chloride-pentane.

Accordingly we proceeded to examine in detail the volatiles in the Toluene Fractions from pyridine and clathrate extraction from both Devco and K-seam coals.

For Devco coal, the very similar traces are shown in the accompanying figures (ion chromatograms) and detailed in the data Tables of Appendix I-5.

The assignments are based on retention indices and a series of standards (naphthalene, phenanthrene, anthracene and chrysene) have been added.

Clearly, no significant differences in the components in the toluene phases from two samples are revealed. Based on this data, it suggested that the predominantly physical nature of the clathration phenomenon is well established, and that the measurement of catalytic activity in the clatharate phase can be made by gcms and grimetric study of the stripping solvent.

Figure 6.0 Gc/ms:
Sample 10-42-1-1
Toluene layer solubles
METHANE CI

CLATHRATE

(Devco Coal)

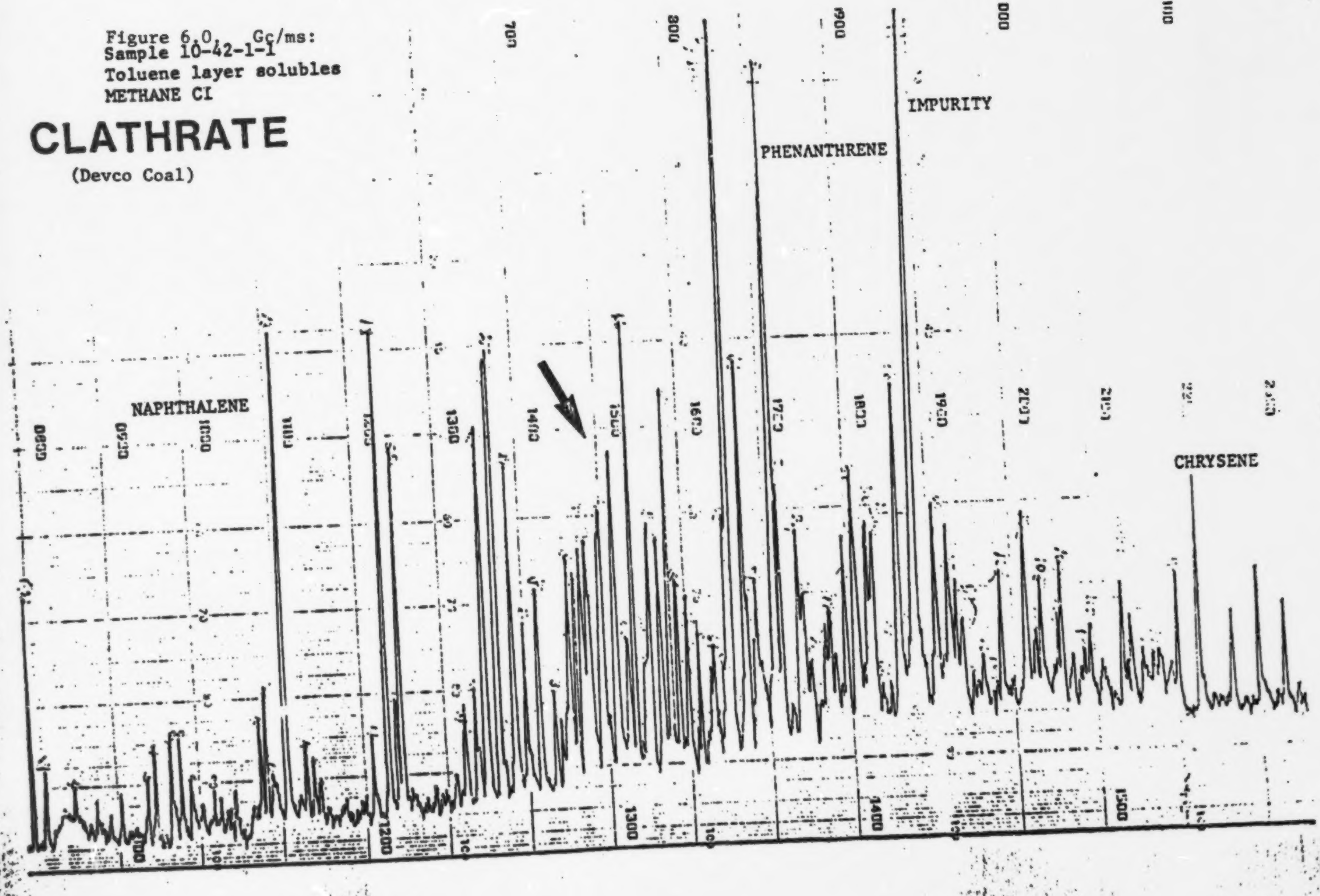
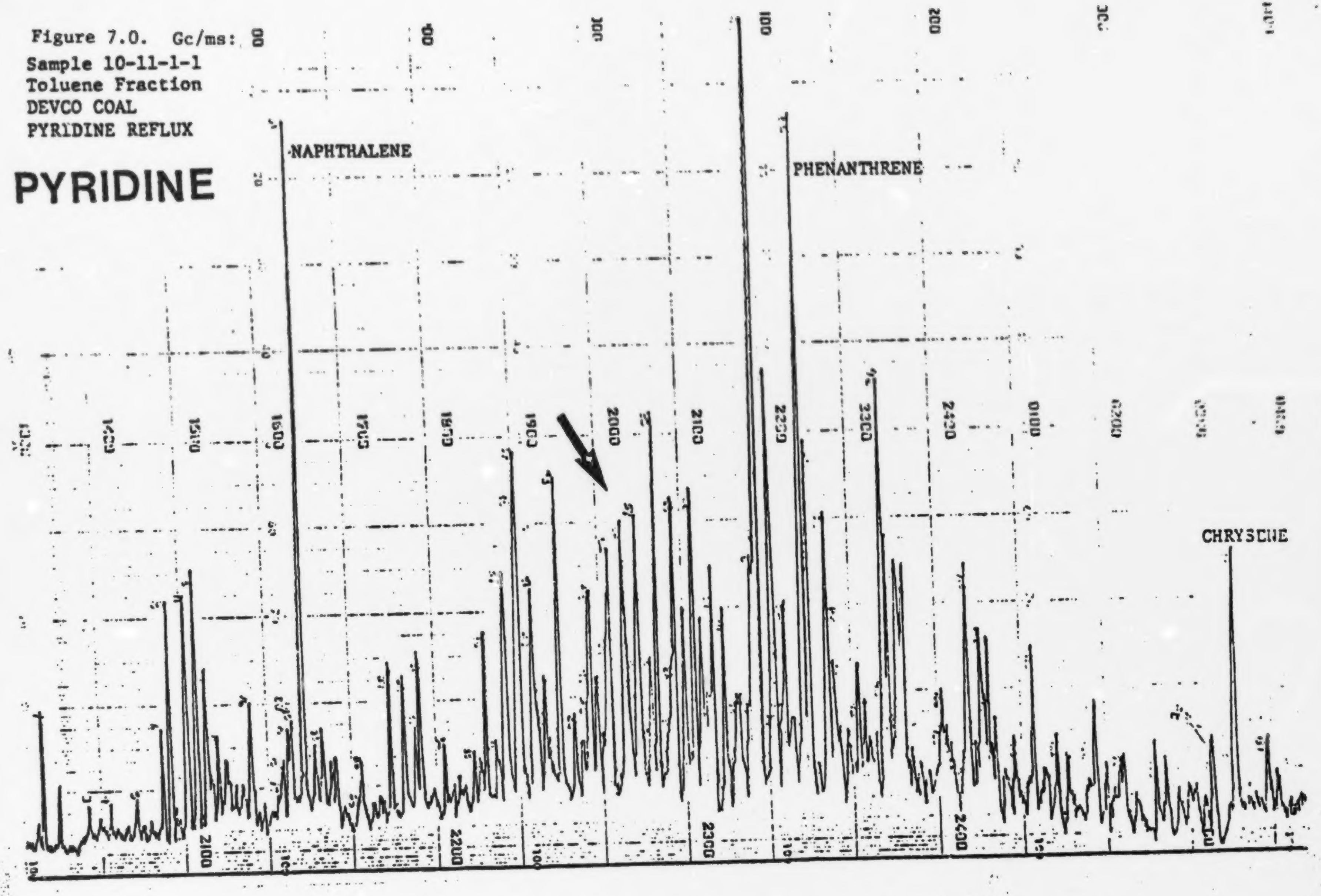


Figure 7.0. Gc/ms:
Sample 10-11-1-1
Toluene Fraction
DEVCO COAL
PYRIDINE REFLUX

PYRIDINE



4.0 PROGRESS AND PROJECTION

The substantial refinement in the techniques of assessing the liquid clathrate (biphasic solvent-salt) systems achieved during the 1984-85 Contract Year has allowed two significant developments in the progress of the overall project.

(i) Definitive assessment of the physical character of the dissolution and the achievement of the necessary analytical precision to assign changes in solvent fraction mass and character to catalytic upgrading.

(ii) Establishment of model catalytic processes in clathrate systems and observation of discrete measureable enhancement of coal mobilization through application of hydrogen overpressure and addition of Lewis acid and metal co-ordination complex agents.

Accordingly, catalyst and promotor development especially in the content of air stable clathrating agents can be specifically pursued with the objective of both increasing net mobilization and enhancing the volatility of the low severity product.

APPENDIX I-1

RESULTS OF APPLICATION OF LIQUID CLATHRATE TO SELECTED COALS

Note: The presentation of data in Appendix I-1 has been organized chronologically in view of changing conditions, solvents and coal charge during the contract year.

May 1984

Table I-1-1. Results of Reactions of Various Coals with Clathrate.

Exp.	Coal	Conditions (No H_2 or catalyst unless listed. 100 ml clath., 10g coal unlisted.)	Wt. of Sol. Hydrocarbons (g) from 10.0g of Coal					
			A (Toluene)	B($CHCl_3$) (Coal)	C($CHCl_3$) (Clathrate)	B (cold pyr.) (Coal)	C (cold pyr.) (Clathrate)	Total Sol.
13-2	Quinsam	20 hr, 70°C	0.021	0.012	0.039	1.167	0.413	1.652
14-1	Mary L (Alabama)	" "	0.083	0.0364	0.184	1.429	1.504	3.236 *
12-3	KB/Devco	4:1 mixture, 20 hr, 70°C	0.100	0.007	0.096	0.879	1.792	2.874
14-2	Mary L	20 hr, 70°C	0.119	0.029	0.182	0.920 †	1.230	2.480†
10-15	Devco	" "	0.135	0.116	0.112	2.030	1.444	3.837
10-16	Devco	" "	0.133	0.035	0.200	1.053	2.575	3.996
10-17	Devco	" "	0.125	0.032	0.213	1.613	1.967	3.950
10-18	Devco	" "	0.128	0.072	0.142	1.587	1.832	3.761
10-19	Devco	" "	0.120	0.049	0.144	1.577	1.950	3.840
10-20	Devco	" "	0.124	0.039	0.145	1.398	1.489	3.195
15-1	Granby	" "	0.041	0.013	0.095	0.500	1.489	2.138
15-2	Granby	" "	0.048	0.019	0.100	0.513	1.807	2.487
15-5	Granby	" "	0.072	0.026	0.130	0.431	1.543	2.202
17-1	High Temp. Devco	" " (5.12g reacted)	0.088	0.030	0.315	0.236	4.540	5.209
18-1	High Temp. K-seam	" " (5.75g reacted)	0.081	0.028	0.226	0.479	1.543	2.357

† Sample lost during vacuum distillation

* Indicates experiments in which significant pyridine HCl inclusion may have occurred.

Table I-1-2. Results of Reactions of Various Coals with Clathrate.

Experiment	Coal	Conditions: (No H_2 or catalyst unless listed. 100 ml clathrate, 10 g coal)	Weight of Sol. Hydrocarbons (in g) from 10 g of Coal					
			A (Toluene)	$B(CHCl)_3$ (Coal)	$C(CHCl)_3$ (Clathrate)	B(cold pyr.) (coal)	C(cold pyr.) (clath.)	Total Sol.
16-2	Balmer H	20 hr, 70°C	0.122	0.046	0.154	0.108	0.134	0.564
16-3	Balmer H	20 hr, 70°C	0.089	0.082	0.148	0.150	0.127	0.596
18-2	High Temp. K-seam	Cold pyridine extraction	(4.80 g ex toluene soluble material)					3.058
17-2	High Temp. Devco	Cold pyridine extraction	(4.28 g ex toluene soluble material)					2.625
10-21	Devco	20 hr, 70°C, centrifuge separated	0.183	0.025	0.064	0.277	0.227	0.776
10-22	Devco	20 hr, 70°C, repeated extractions	0.235	0.066	0.340	0.442	0.876	1.752
2-53	K-seam	20 hr, 70°C, repeated extractions	0.219	0.076	0.450	0.371	0.348	1.526
10-23	Devco	10g Devco, 2g $CpMn(CO)_3$ and H_2	) See Table I-1-3					
10-24	Devco	10g Devco, 2g $CpMn(CO)_3$, no H_2	)					
14-3	Mary Lee	Repeated extractions	0.264	0.067	0.403	~0.8	0.629	~2.1
10-25	Devco	Pre-extracted with pyridine (0.725g dissolved)	0.054	0.082	0.085	0.690	0.084	0.995

June 1984.

Table I-1-3. Catalyst ($C_5H_5Mn(CO)_3$) Experiments with Devco Coal

Reaction	Toluene Solubles	$CHCl_3$ Solubles		Pyridine Solubles		Insolubles		Total		Overall Total
		Clathrate	Coal	Clathrate	Coal	Clathrate	Coal	Solubles	Insolubles	
#10-23	0.830g	0.564	0.281	0.206	0.587	0.110	9.255	2.468	9.365	11.833
#10-24	0.921g	0.466	0.261	0.150	0.985	0.047	8.577	2.783	8.624	11.407
Mn conc.	16.3%	10.2%	2.31%	155ppm	36ppm	139ppm	26ppm			
Mn correction	-.558g	-.176	-.022	-	-	-	-	-.756	-	
Corrected yields	0.363	0.290	0.239	0.150	0.985	0.047	8.577	2.027	8.624	10.651

Mn in Devco coal is 152ppm.

July 1984.

Table I-1-4. Results of Reactions of Various Coals with Clathrate.

Experiment	Coal	Conditions: (No H_2 or catalyst unless listed. 100ml clathrate, 10g coal)	A (Toluene)	$B(CHCl)_3$ (Coal)	$C(CHCl)_3)$ (Clathrate)	B(cold pyr.) (Coal)	C(cold pyr.) (Clath.)	Total Sol.
10-28	Devco	1 hr sonication	0.031	0.010	0.018	0.642	0.018	0.719
10-29	Devco	2g MeI added	0.092	0.087	0.090	0.827	0.170	1.266
10-30	Devco	sonicate pyr. sols. instead of stir	0.087	0.055	0.122	1.020	0.169	1.453
10-31	Devco	sonicated during reaction	0.027	0.021	0.029	0.843	0.055	0.975
10-32	Devco	clathrate pyridine reflux res. (3.51g)	0.014	0.002	0.082	0.128	0.055	0.281
11-[illegible]-3	K-seam	5g coal, overnight pyridine reflux				0.650		0.650
11-14-3	Mary L[illegible]	" " "				1.210		1.210
11-10-9	Devco	" " "				1.024		1.024
17-3	Devco	clathrate H.T. liq. filter cake	0.100	0.036	0.268	0.278	1.618	2.300
18-3	K-seam	" " " "	0.070	0.067	0.594	0.264	2.079	2.852
10-33	Devco	$(Me)_4NI$ m-xylene, sequential (3 passes)	0.204	0.037	0.229	0.698	0.825	1.993
2-55	K-seam	" " "	0.205	0.094	0.203	0.299	0.474	1.275
11-10-10	Devco	10g Devco refluxed in pyr..				1.844		1.844
10-36	Devco	1.78g pyr. soluble extract in clathrate	0.195	0.023	0.262			
10-37	Devco	85°C, 20 hr clathration	0.164	0.093	0.091	0.897	0.421	1.670
10-38	Devco	70°C, 20 hr clathration	0.080	0.045	0.070	1.040	0.173	1.408

August 1984.

Table I-1-5. Results of Reactions of Various Coals with Clathrate.

Experiment	Coal	Conditions: Pr$_4$NI-toluene clathrate, 20 hr, 10g of unless stated	A (Tol.)	B(CHCl)$_3$ (Coal)	C(CHCl)$_3$) (Clath.)	B(cold pyr.) (Coal)	C(cold pyr.) (Clath.)	Total Sol.	Total Insol.
10-39	Devco	Pr$_4$NI-metaxylene clathrate, 3 passes, 85°C	0.220	0.058	0.309	0.389	1.279	2.255	6.868
10-40	Devco	Coal preheated to 300°C in N$_2$ stream, 85°C clathration	0.083	0.111	0.131	1.047	0.135	1.567	9.711
10-41	Devco	HCl-extracted coal, 85°C	0.092	0.128	0.242	1.061	0.254	1.777	7.941
2-57	K-seam	Coal preheated to >300°C in N$_2$ stream 85°C (sample coked so no good)	0.053	0.053	0.079	0.135	0.159	0.479	10.432
11-2-11	K-seam	20g refluxed with pyridine				2.432		2.432	17.681
11-16-1	Balmer H	10g refluxed with pyridine				0.262		0.262	9.762
11-19-1	Balmer L	10g refluxed with pyridine				0.627		0.627	9.359
11-7-1	Merritt	10g refluxed with pyridine				0.432		0.432	9.242
11-14-2	Mary Lee	10g refluxed with pyridine				2.140		2.140	7.624
10-44	Devco	Devco clathrated at 100°C, one pass	0.167	0.145	0.139	0.843	0.531	1.825	7.585
16-4	Balmer H	85°C, single pass clathration	0.112	0.180	0.165	0.068	0.143	0.668	9.314
19-1	Balmer L	85°C, single pass clathration	0.127	0.131	0.128	0.150	0.291	0.827	9.191
2-58	K-seam	Coal preheated to 300°C in N$_2$ stream 9.21g coal, 85°C clathration	0.132	0.056	0.061	0.183	0.392	0.824	7.524

September 1984.

Table I-1-6. Results of Reactions of Various Coals with Clathrate.

Experiment	Coal	Conditions: Pr_4NI-toluene clathrate, 20 hr, 10g of coal unless stated	A (Tol.)	B$(CHCl)_3$ (Coal)	C$(CHCl)_3$) (Clath.)	B(cold pyr.) (Coal)	C(cold pyr.) (Clath.)	Total Sol.	Total Insol.
10-45	Devco	Bu_4NI mixed xylenes 120°C	0.192	0.093	2.570[*]	--	--	--	--
10-46	Devco	Bu_4NI mixed xylenes 100°C	0.136	0.217	2.806[*]	0.477	0.807	4.443	7.572
10-47	Devco	ηPr_4NI mixed xylenes 120°C	0.166	0.128	0.183	1.191	0.398	2.066	6.148
10-48	Devco	ηPr_4NI mixed xylenes 100°C	0.143	0.009	0.183	0.528	0.393	1.256	7.667
10-49	Devco	ηPr_4NI mixed xylenes, $(CH_3)_3Al$, 120°C	0.128	0.094	0.197	0.328	0.424	1.171	7.405
10-50	Devco	ηPr_4NI mixed xylenes 120°C	0.124	--	0.157	--	0.533	--	--
10-50[ii]	Devco	ηPr_4NI mixed xylenes 120°C	0.049	0.061	0.165	0.204	0.657	1.950	6.574
11-10-11	Devco	20 hr pyridine reflux[**] (10g)	--	--	--	2.018	--	2.018	7.212
11-10-12	Devco	20 hr pyridine reflux[**]	--	--	--	2.362	--	2.362	6.953
11-20-2	Anthracite (Canmore)	20 hr pyridine reflux (5g)	--	--	--	<negligible>	--	<negligible>	5.059

[*] Run abandoned, ηBu_4NI distributes in chloroform solubles. Further development of workup procedure required for this salt.

[ii] Second pass.

[**] For partition experiments.

Table I-1-7. Preliminary Tetralin Extraction Experiments

			Clathrate Layer (C)			Residue (B)				
Experiment	Conditions	Tetralin Layer	Chloro. Sol.	Pyr. Sol.	Insol.	Chloro. Sol.	Pyr. Sol.	Insol.	Total Sol.	Total Insol.
2-60	100 ml tetralin clathrate, 180°C, tetrapropyl ammonium chloride, 10 g (K-seam), (20 hours)	0.155	0.254	0.461	0.932	0.265	0.368	7.650	1.503	8.582
10-58	120°C, 10 g Devco (20 hours)	0.046	0.115	0.219	0.606	0.044	0.328	7.224	0.752	7.830
10-59	180°C, 10 g Devco (20 hours), 2 g $AlCl_3$	0.139	0.158	0.592	2.314	0.090	0.335	4.694	1.314	7.008

December 1984.

Table I-1-8. Preliminary Tetralin Extraction Experiments

Exper-iment	Conditions	Tetralin/ Xylene Layer	Clathrate Layer (C) Chloro. Sol.	Clathrate Layer (C) Pyr. Sol.	Clathrate Layer (C) Insol.	Residue (B) Chloro. Sol.	Residue (B) Pyr. Sol.	Residue (B) Insol.	Total Sol.	Total Insol.
10-59	180°C, 10 g Devco, No H_2 (20 hours), 2 g $AlCl_3$, tetralin	0.139	0.158	0.592	2.314	0.090	0.335	4.694	1.314	7.008
10-60	120°C, 10 g Devco, 1 atm H_2 100 mg $RuCl_2[(C_6H_5)_3P]_3$ xylenes, 20 hours	0.117	0.207	0.476	1.408	0.143	0.554	7.247	1.497	8.655
10-61	120°C, 10 g Devco 0.2 ml $TiCl_4$, H_2 1 atm xylenes, 20 hours	0.199	0.194	0.603	1.097	0.111	0.433	6.324	1.540	7.421
10-62	120°C, 10 g Devco 0.3 ml $SnCl_4$, H_2 1 atm xylenes, 20 hours	0.200	0.144	0.638	0.697	0.121	0.489	7.405	1.592	8.102
10-63	140°C, 10 g Devco xylenes, 20 hours	0.184	0.235	0.696	0.400	0.129	0.602	6.959	1.846	7.359
10-64	120°C, 10 g Devco xylenes, 20 hours CONTROL	0.170	0.182	0.581	0.176	0.170	0.234	9.042*	1.337*	9.62
10-65	120°C, 10 g Devco xylenes, 20 hours 2.0 g $AlCl_3$.	0.203	0.185	0.338	0.158	0.119	0.886	7.272	1.55	7.61
10-66	120°C, 10 g Devco xylenes, 20 hours, 2.0 g $AlCl_3$, 1 atm H_2	0.213	0.152	0.472	0.192	0.109	0.790	7.092	1.737	7.284
10-67	120°C, 10 g Devco xylenes, 20 hours, 100 mg $RuCl_2P_3$. H_2	0.184	0.214	0.723	0.678	0.180	1.070	6.613	2.371	7.291
10-47	120°C, 10 g Devco xylenes, 20 hours (early run)	0.166	0.183	0.398	0.084	0.128	1.191	6.064	2.066	6.148
10-48	100°C, 10 g Devco xylenes, 20 hours, (early run)	0.143	0.183	0.393	0.117	0.009	0.528	7.550	1.256	7.667

January 1985.

Table I-1-9. Preliminary Tetralin Extraction Experiments

Exper-iment	Conditions	Tetralin/ Xylene Layer	Clathrate Layer (C)			Residue (B)			Total Sol.	Total Insol.
			Chloro. Sol.	Pyr. Sol.	Insol.	Chloro. Sol.	Pyr. Sol.	Insol.		
10-64	120°C, xylenes, no H_2	0.170	0.182	0.581	0.176	0.170	0.234	9.042	1.337	9.218
10-65	$AlCl_3$, xylenes, 120°C, no H_2	0.203	0.185	0.338	0.158	0.119	0.886	7.272	1.558	7.430
10-66	$AlCl_3$, xylenes, 120°C, 1 atm H_2	0.213	0.152	0.472	0.192	0.109	0.790	7.092	1.737	7.284
10-67	120°C, xylenes, 100 mg $RuCl_2P_3$, 1 atm H_2	0.184	0.214	0.723	0.678	0.180	1.070	6.613	2.371	7.291
10-68	180°C, xylenes, 2g $AlCl_3$ 500 psi H_2	0.126	0.200	0.774	0.617	0.211	1.205	6.340	2.516	6.957
10-69	180°C, xylenes, 2g $AlCl_3$ 500 psi H_2	0.215	0.239	0.789	0.420	0.253	1.214	5.698	2.710	6.118
				(20 ml clathrate)						
10-70	180°C, xylenes, 500 psi H_2, no $AlCl_3$	0.249	0.180	0.528	1.043	0.267	0.839	6.137	2.063	7.180
10-71	180°C, xylenes, 500 psi H_2, no $AlCl_3$	0.370		No Clathrate		0.397	1.746	5.967	2.513	5.967
10-72	180°C, xylenes, 2g $AlCl_3$, 500 psi H_2, 100mg $RuCl_2P_3$	0.352	0.109*	1.201	0.309	0.212	0.357	6.771	2.231	7.080
10-73	180°C, xylenes, 2g $AlCl_3$, 500 psi H_2, 100mg $RuCl_2P_3$	0.267	0.181	0.817	0.118	0.183	1.137 0.196**	6.388	2.781	6.506

*spillage

**second cold pyridine extraction

February 1985.

Table I-1-10. Preliminary Tetralin Extraction Experiments

Experiment	Conditions	Tetralin/ Xylene Layer	Clathrate Layer (C)			Residue (B)			Total Sol.	Total Insol.
			Chloro. Sol.	Pyr. Sol.	Insol.	Chloro. Sol.	Pyr. Sol.	Insol.		
10-74	7.5g coal, 120°, xylenes, 500 psi H_2, 100 mg $RuCl_2P_3$	0.160	0.160	0.664	0.181	0.076	0.482	5.130	1.542	5.311
10-75	7.5g coal, 500 psi H_2, No catalyst, No $AlCl_3$, 120°	0.110	0.166	0.630	0.205	0.084	0.505	5.493	1.495	5.698
10-76	7.5g coal, 500 psi H_2, 120° 100 mg $RhClP_3$, No $AlCl_3$	0.206	0.194	0.689	0.210	0.194	0.567	5.205	1.758	5.415
10-77	7.5g coal, 500 psi H_2, 120° 100 mg $RhClP_3$, 2g $AlCl_3$	0.165	0.168	0.476	0.077	0.105	0.513	5.846	1.427	5.923
10-78	7.5g coal, 500 psi H_2, 120° 100 mg $RhClP_3$, No $AlCl_3$	0.149	0.158	0.721	0.221	0.087	0.465	5.522	1.580	5.743
10-79	7.5g coal, 500 psi H_2, 120° No catalyst, No $AlCl_3$	0.148	0.125	0.602	0.201	0.066	0.628	5.356	1.569	5.556
10-80	7.5g coal, 500 psi H_2, 140° 100 mg $RhClP_3$, No $AlCl_3$	0.131	0.168	0.869	0.399	0.126	0.746	5.281	2.040	5.680

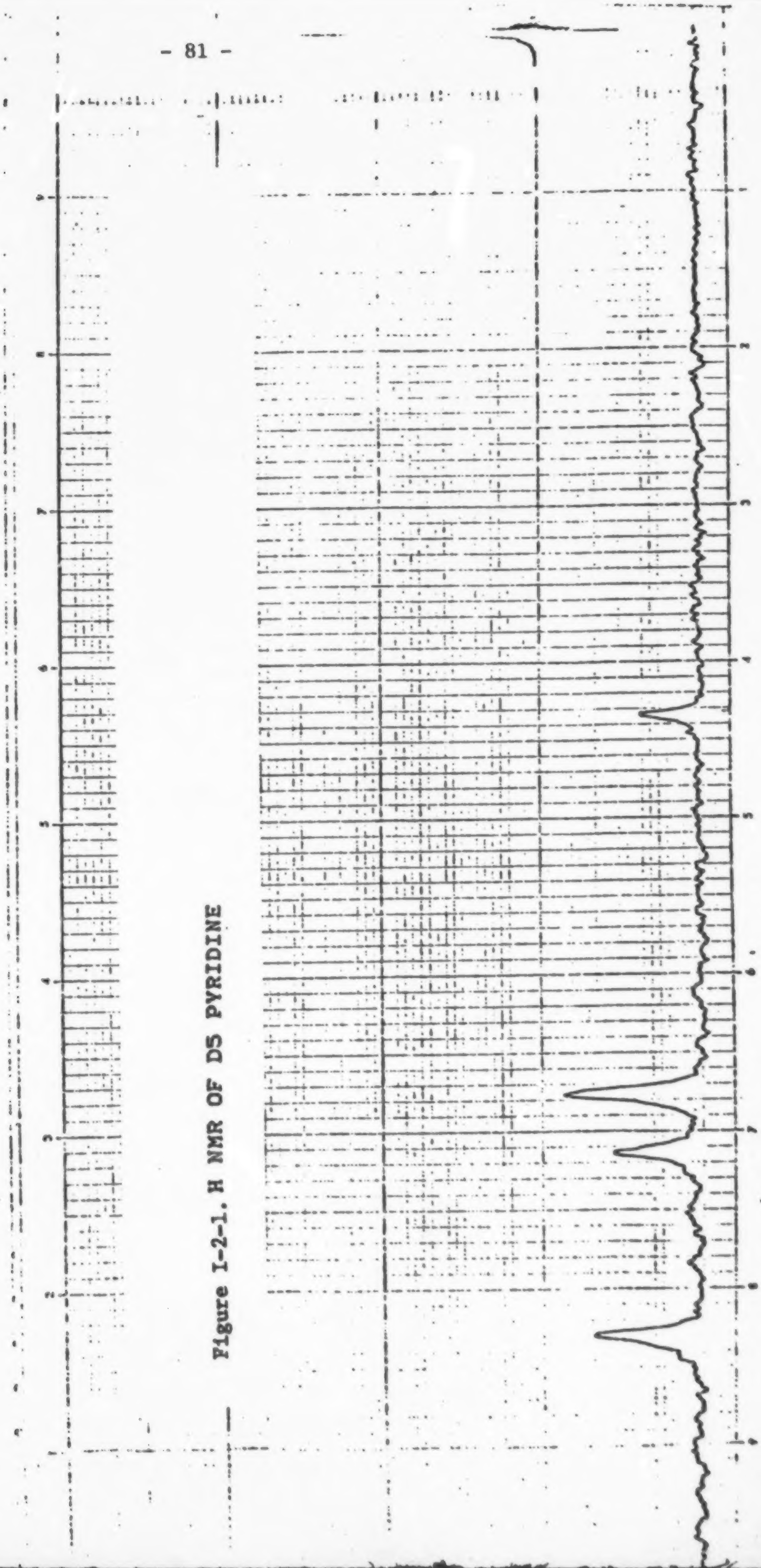


Figure I-2-1. H NMR OF D5 PYRIDINE

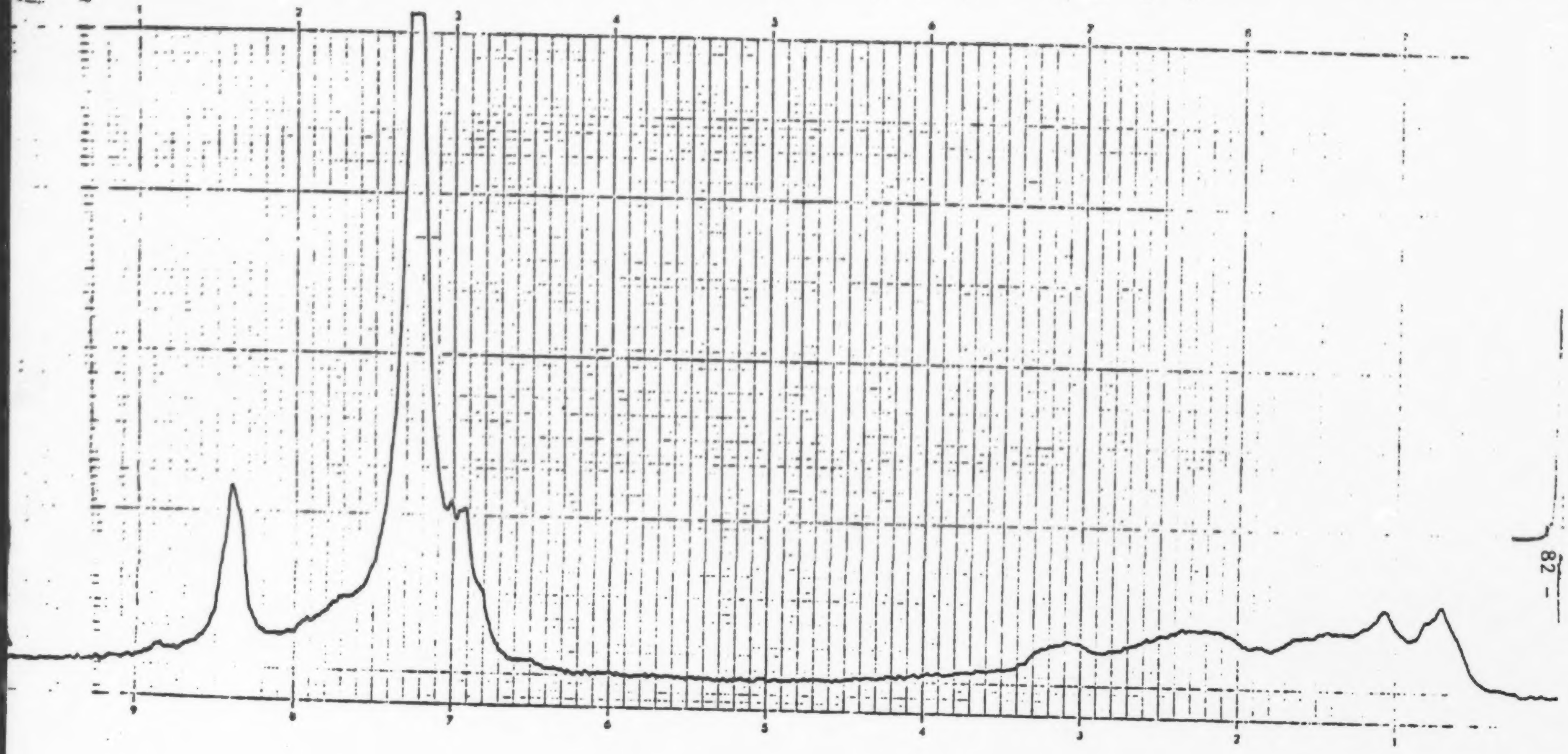
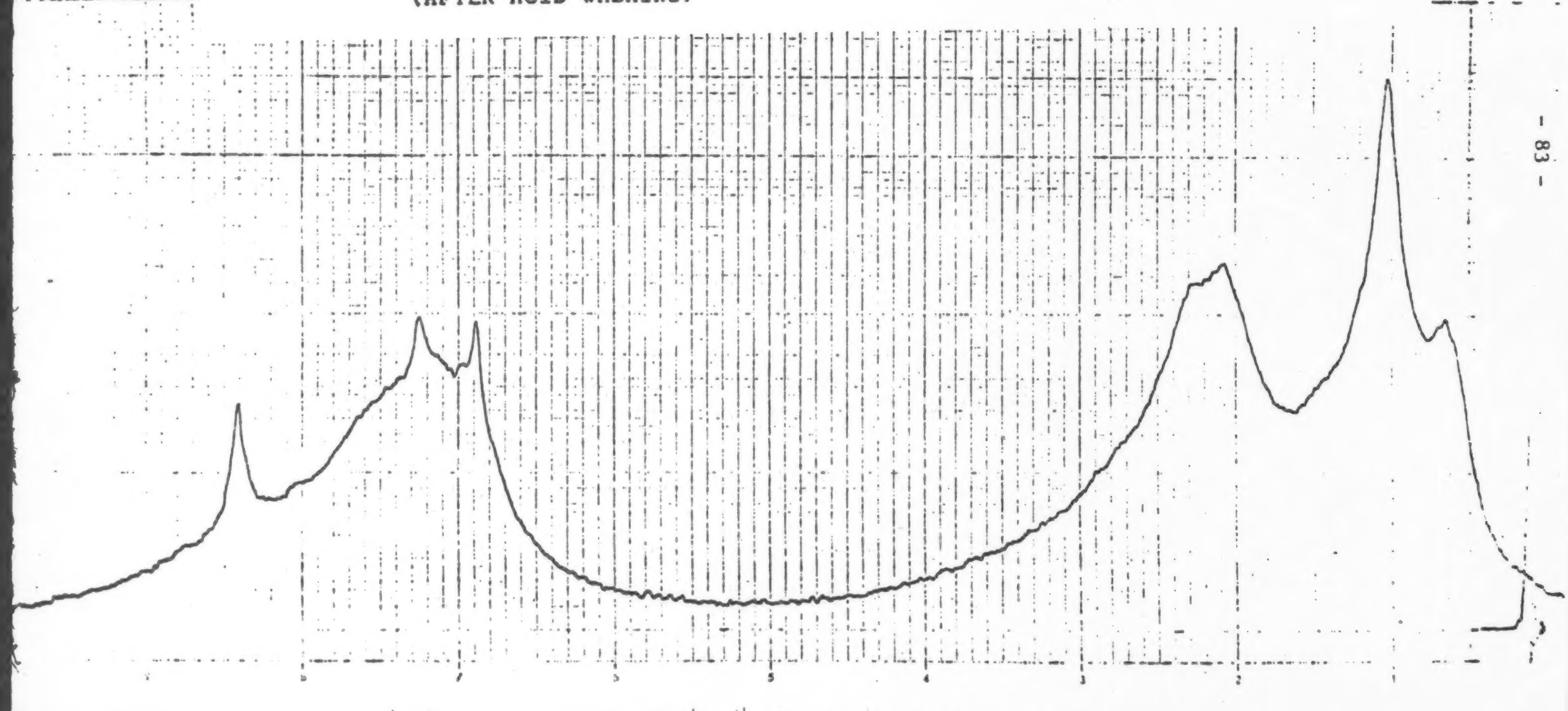


Figure I-2-2. H NMR OF D5 PYRIDINE SOLUTION OF PYRIDINE EXTRACTS OF COAL (NO ACID WASH)

Figure I-2-3. H NMR OF D5 PYRIDINE SOLUTION OF PYRIDINE EXTRACTS OF COAL

(AFTER ACID WASHING)



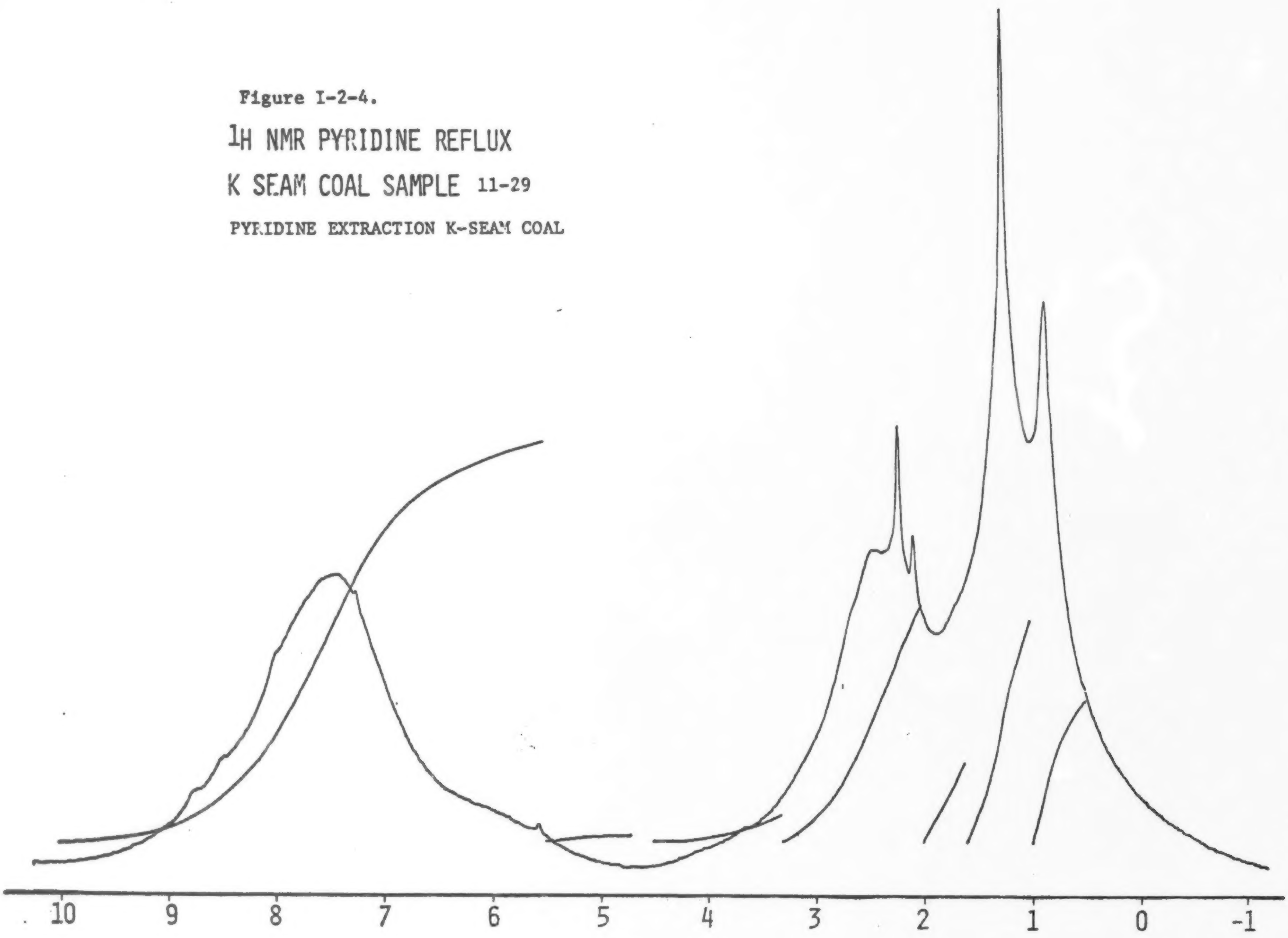


Figure I-2-4.

1H NMR PYRIDINE REFLUX

K SEAM COAL SAMPLE 11-29

PYRIDINE EXTRACTION K-SEAM COAL

Figure I-2-5.
^1H NMR PYRIDINE REFLUX
K SEAM COAL SAMPLE 11-2-11
250 MHz $CDCl_3$ Lock $AsCl_3$

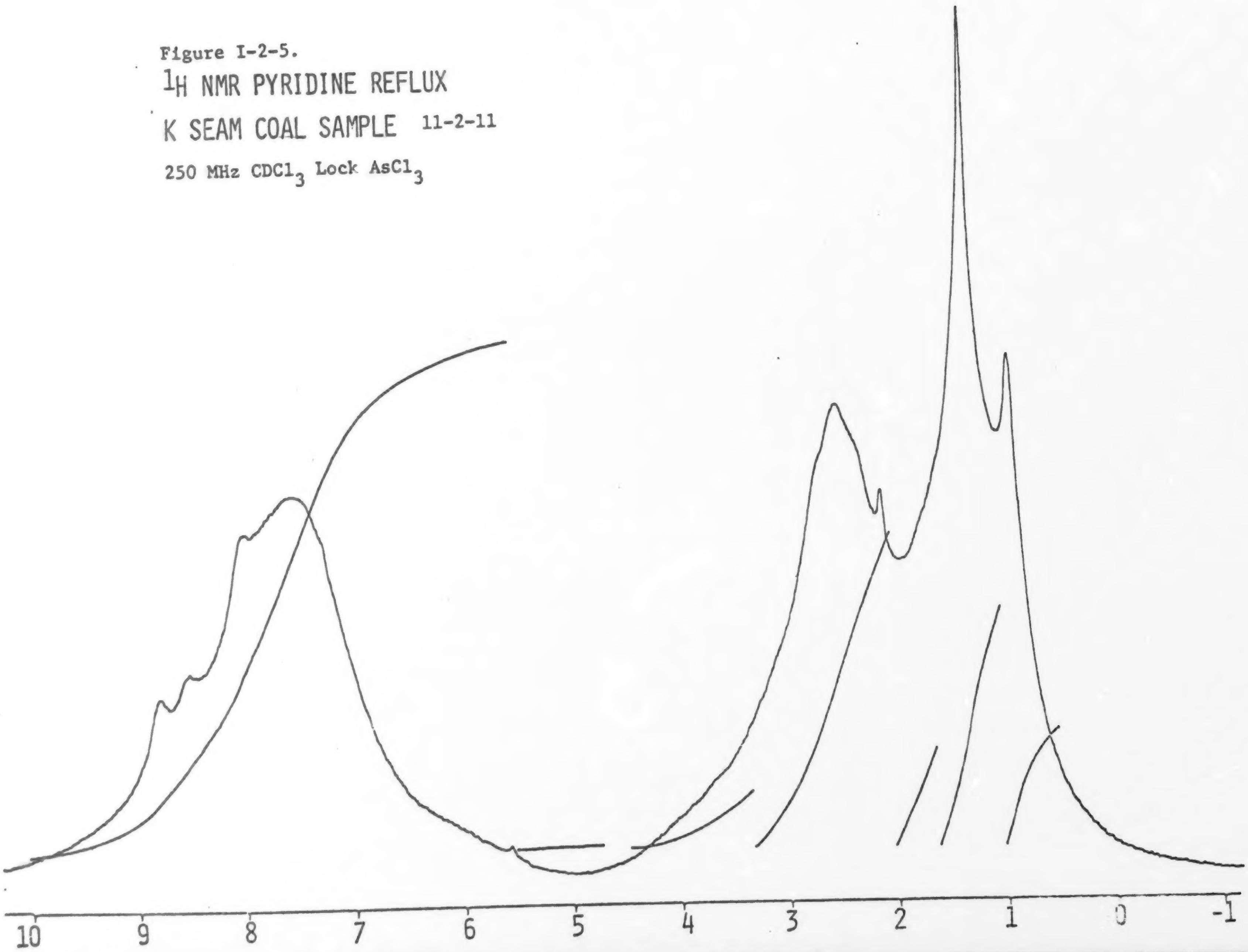
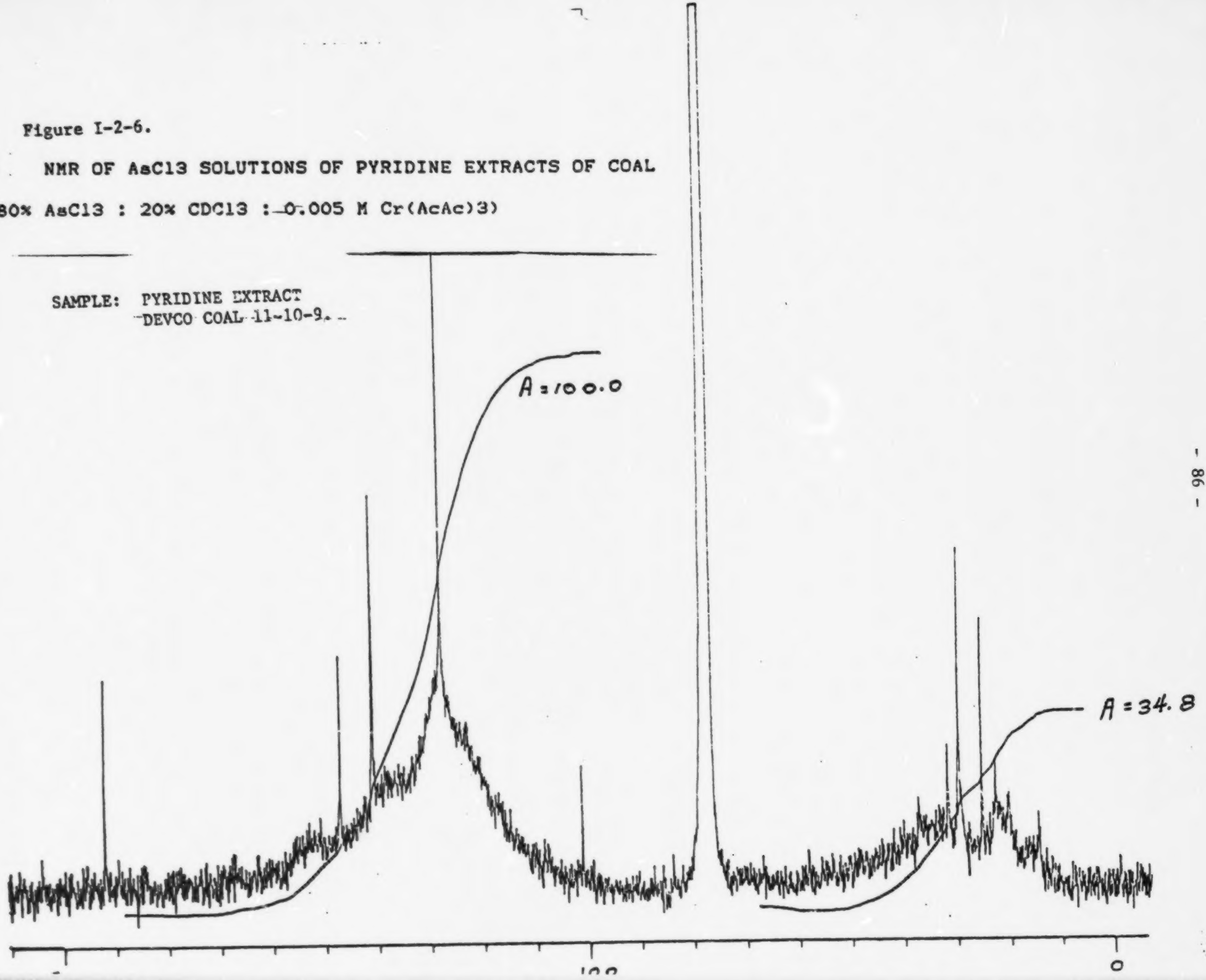


Figure I-2-6.

^{13}C NMR OF AsCl3 SOLUTIONS OF PYRIDINE EXTRACTS OF COAL

(80% AsCl3 : 20% CDCl3 : 0.005 M Cr(AcAc)3)

SAMPLE: PYRIDINE EXTRACT
DEVCO COAL 11-10-9.



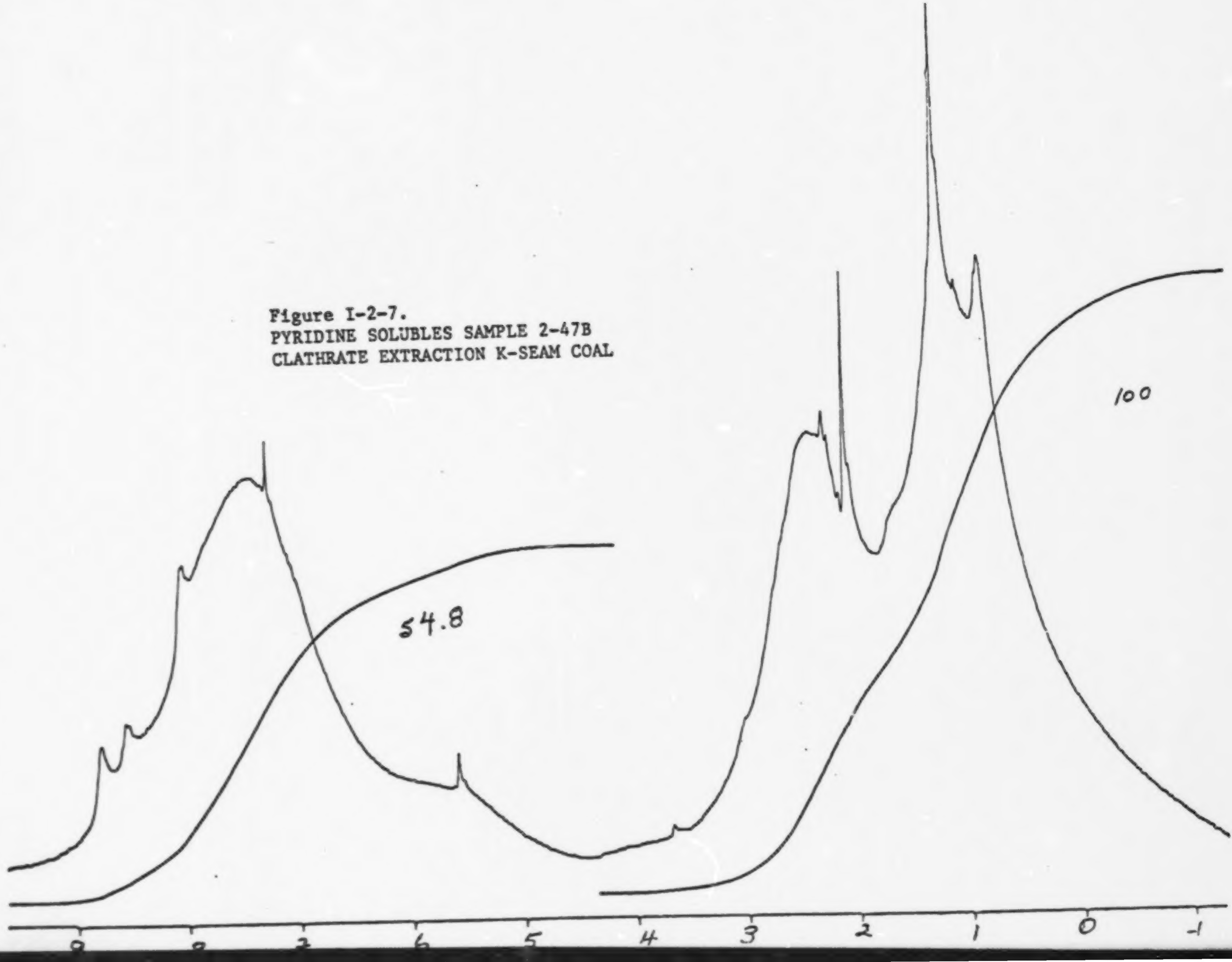
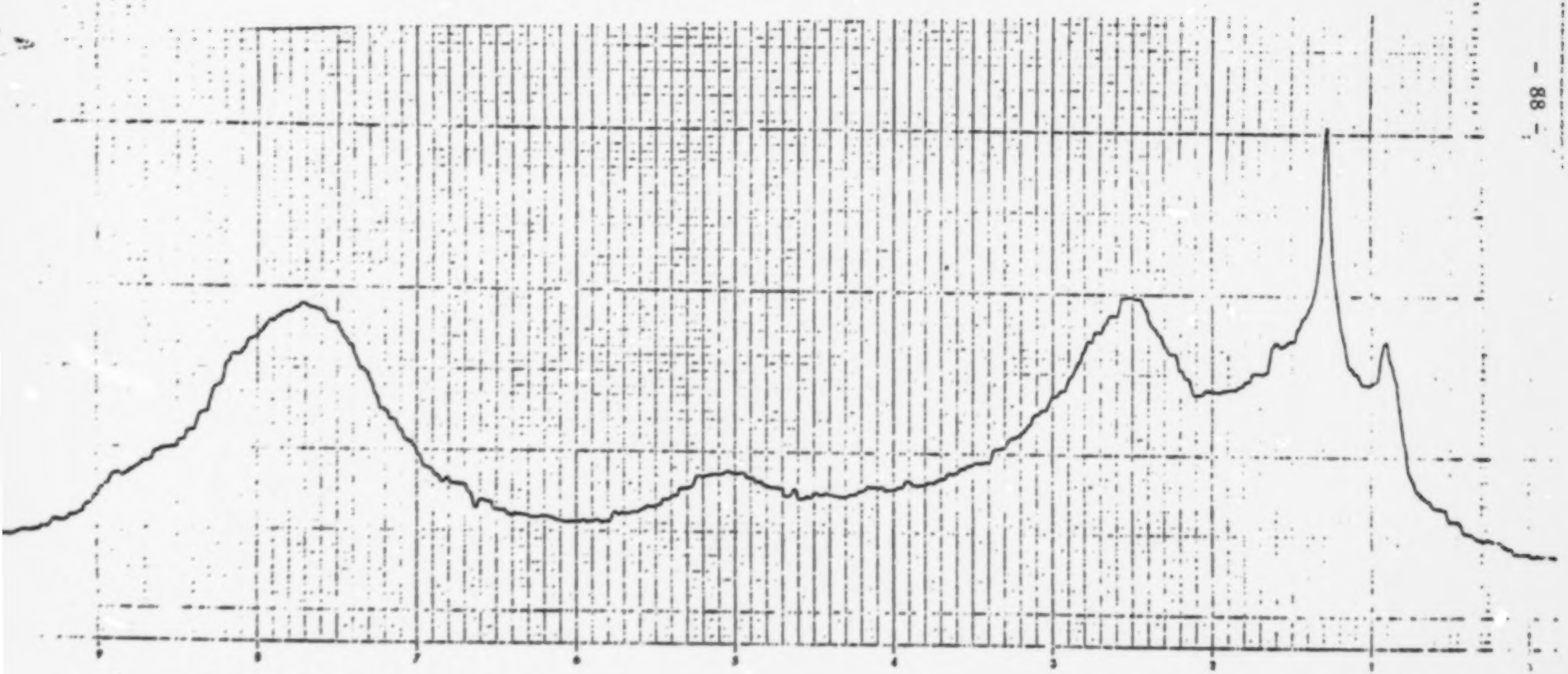
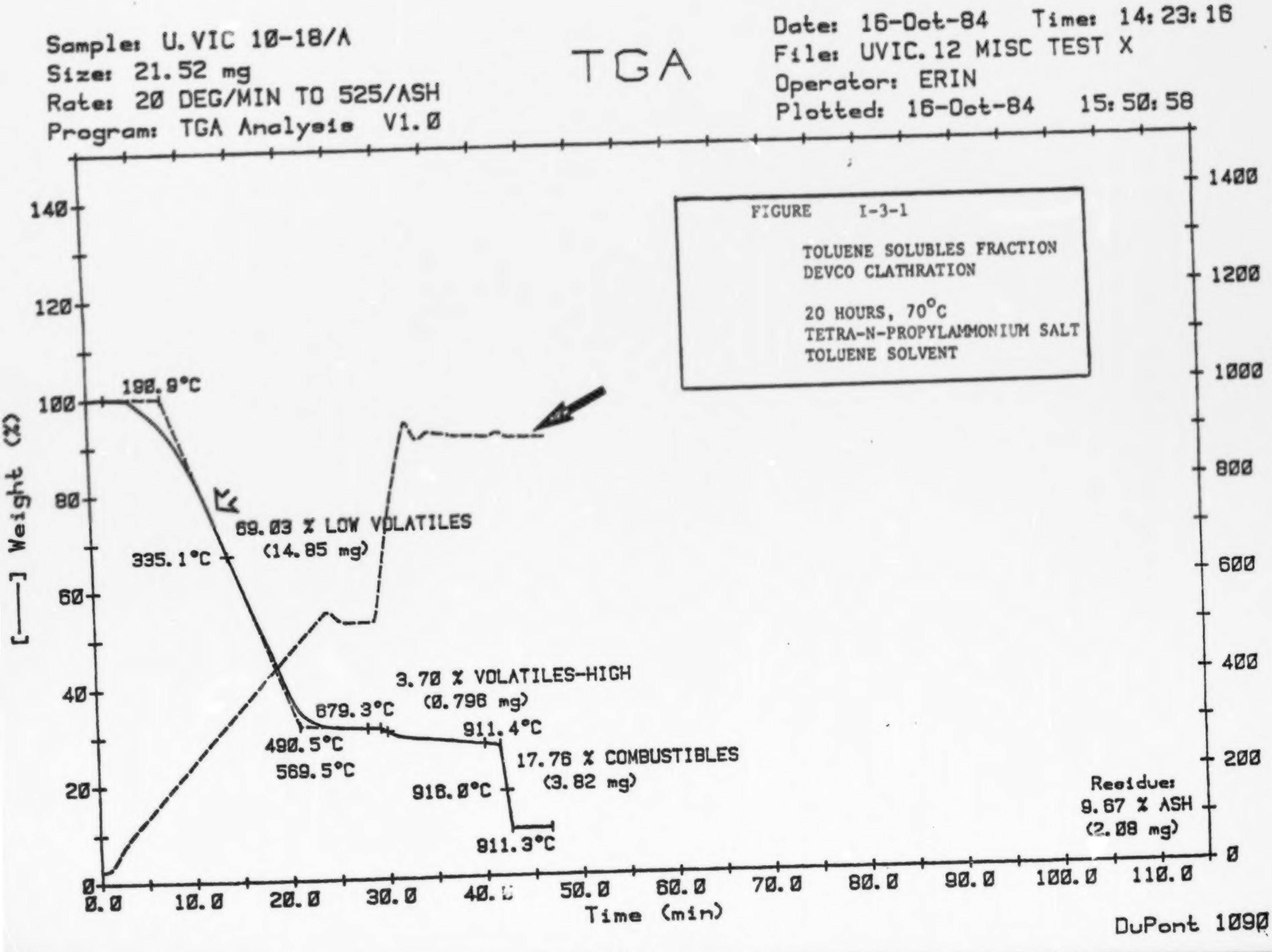


Figure I-2-7.
PYRIDINE SOLUBLES SAMPLE 2-47B
CLATHRATE EXTRACTION K-SEAM COAL

Figure I-2-8.

H NMR OF AsCl3 SOLUTIONS OF PYRIDINE EXTRACTS OF COAL





Sample: U.VIC 10-18/A
Size: 21.52 mg
Rate: 20 DEG/MIN TO 525/ASH
Program: TGA Analysis V1.0

Date: 16-Oct-84 Time: 14:23:16
File: UVIC.12 MISC TEST X
Operator: ERIN
Plotted: 16-Oct-84 15:50:58

FIGURE I-3-1

TOLUENE SOLUBLES FRACTION
DEVCO CLATHRATION

20 HOURS, 70°C
TETRA-N-PROPYLAMMONIUM SALT
TOLUENE SOLVENT

Sample: U.VIC 2-49A
Size: 21.26 mg
Rate: 20 DEG/MIN TO 525/ASH
Program: TGA Analysis V1.0

TGA

Date: 25-Jul-84 Time: 14:08:49
File: UVIC.08 MISC TEST IX
Operator: ERIN
Plotted: 25-Jul-84 16:06:04

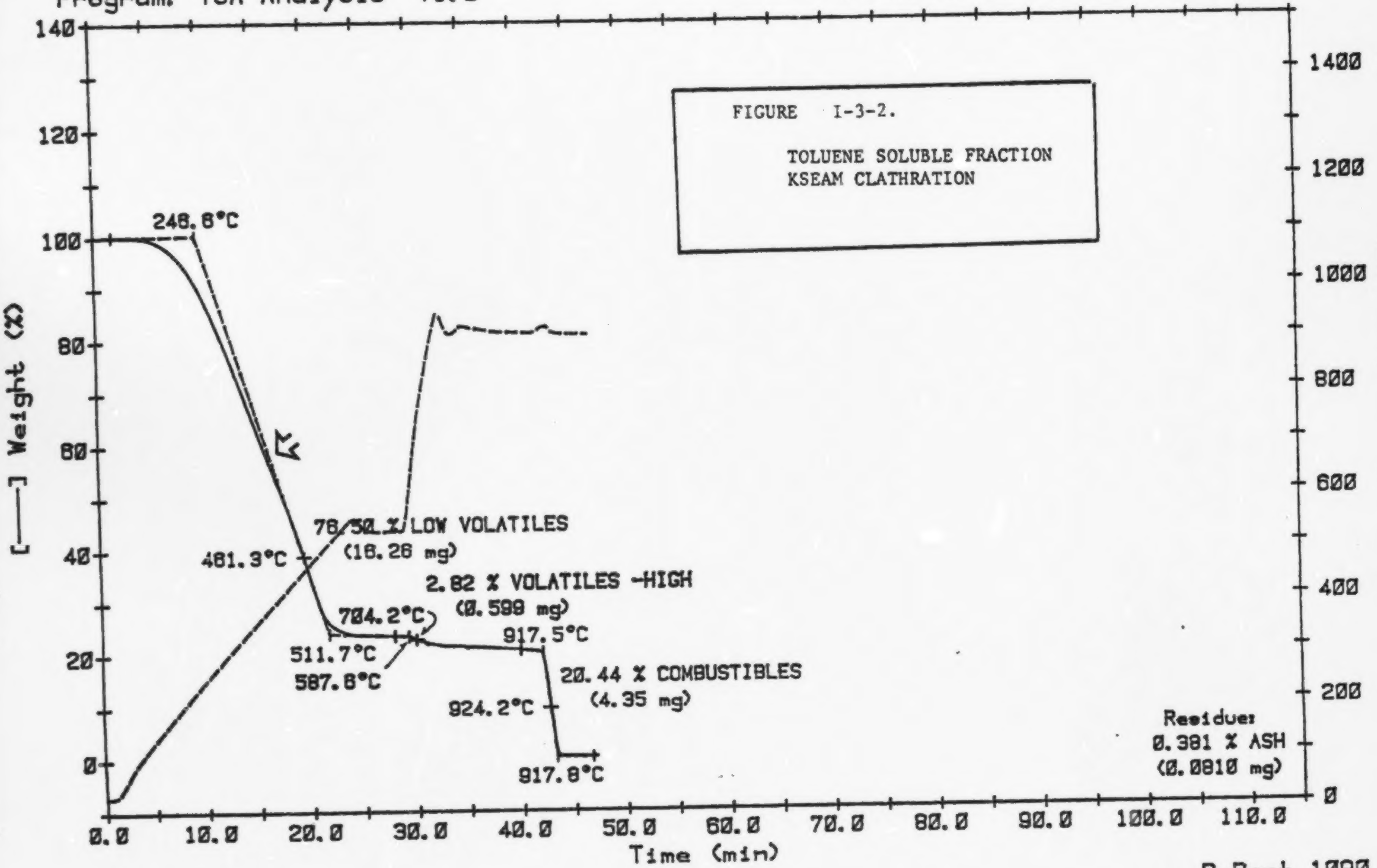


FIGURE I-3-2.

TOLUENE SOLUBLE FRACTION
KSEAM CLATHRATION

DuPont 1090

Sample: 10-51-C
Size: 17.71 mg
Rate: 20 DEG/MIN TO 525/ASH
Program: TGA Analysis V1.0

TGA

Date: 5-Nov-84 Time: 9:47:51
File: UVIC.16 MISC TEST XI
Operator: ERIN
Plotted: 5-Nov-84 11:03:57

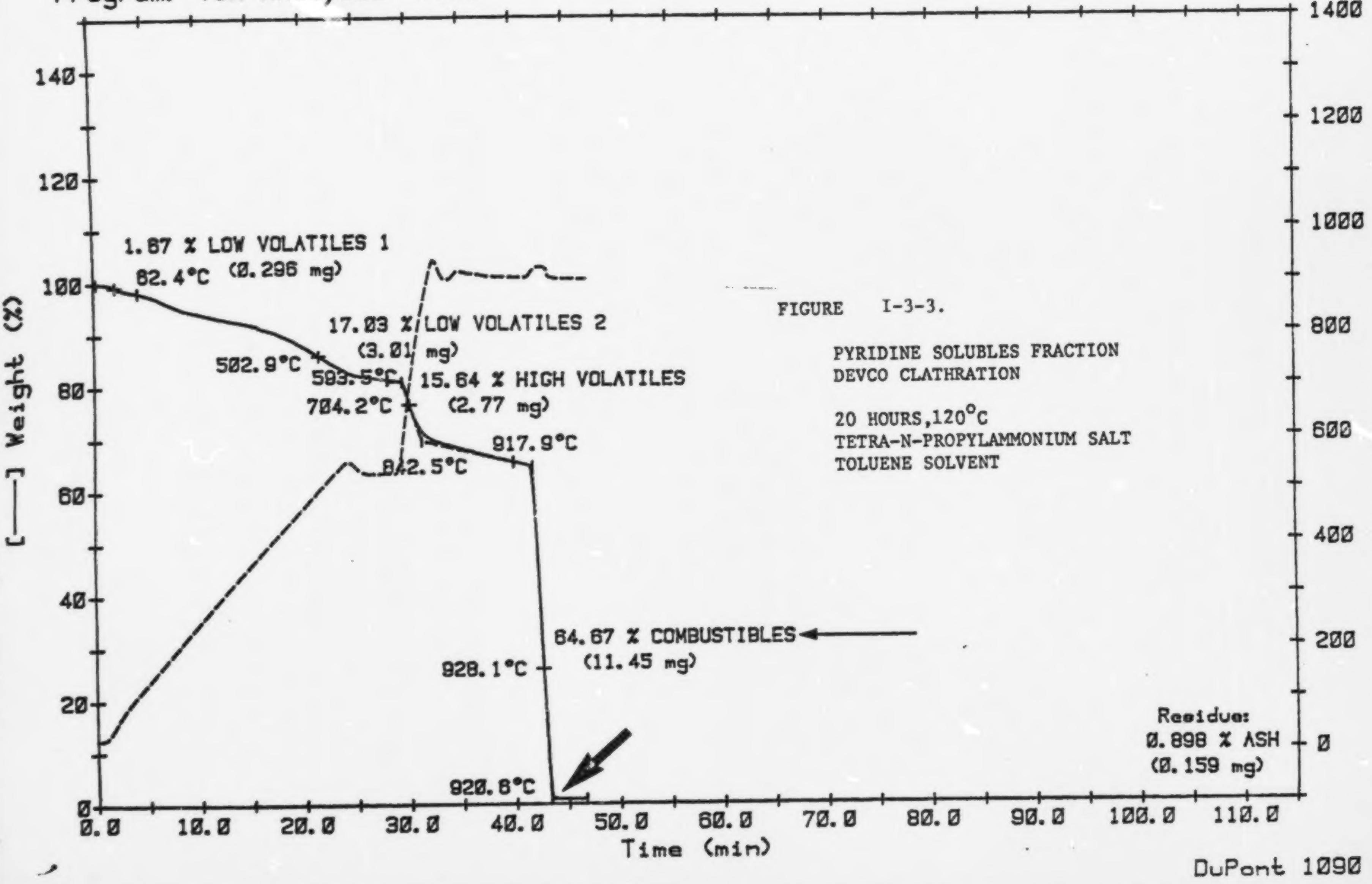


FIGURE I-3-3.

PYRIDINE SOLUBLES FRACTION
DEVCO CLATHRATION

20 HOURS,120°C
TETRA-N-PROPYLAMMONIUM SALT
TOLUENE SOLVENT

Sample: 11-10-11
Size: 18.30 mg
Rate: 20 DEG/MIN TO 525/ASH
Program: TGA Analysis V1.0

TGA

Date: 6-Nov-84 Time: 8:09:33
File: UVIC.19 MISC TEST XI
Operator: ERIN
Plotted: 6-Nov-84 9:30:56

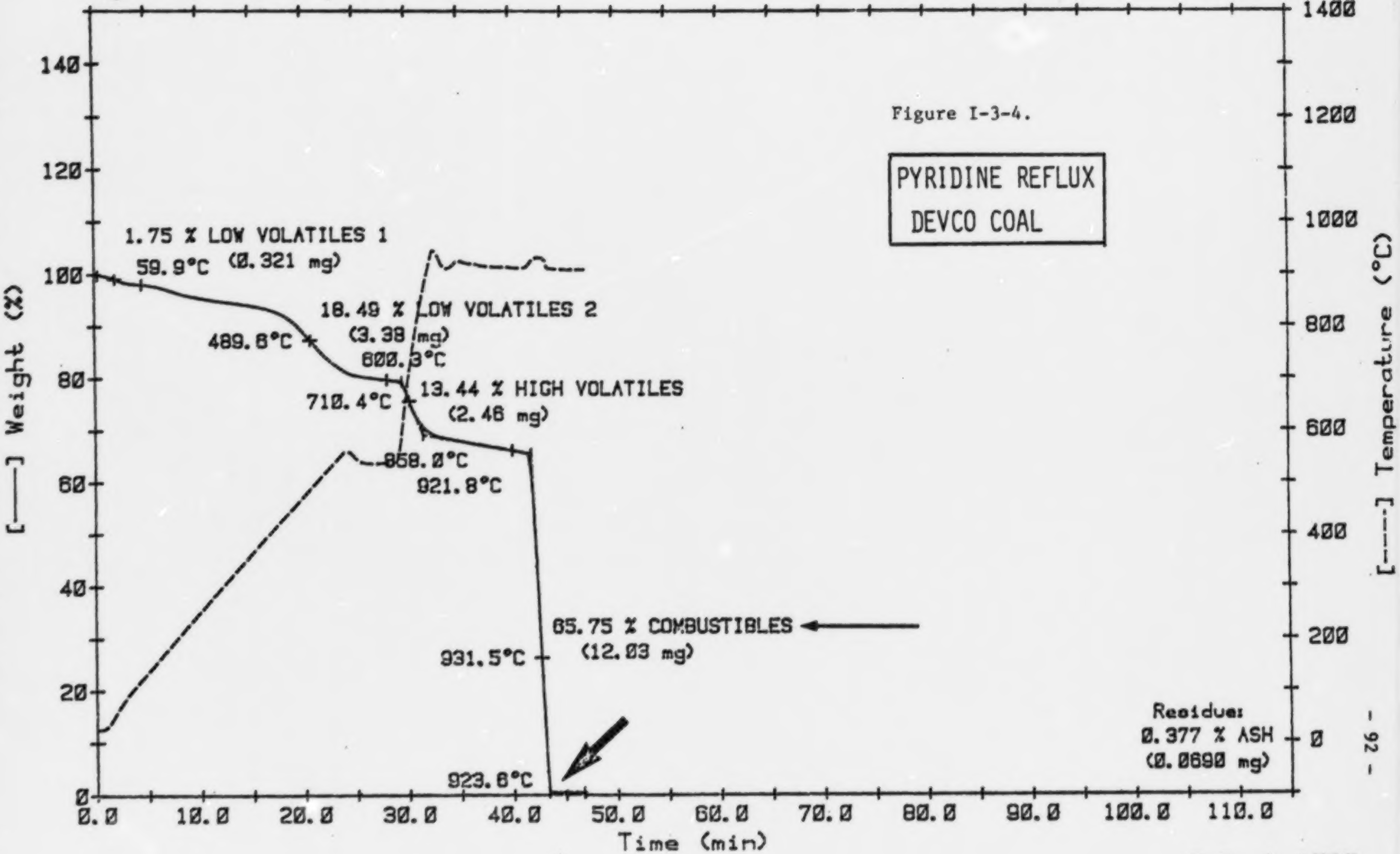


Figure I-3-4.

DuPont 1090

Sample: 11-2-12
Size: 14.97 mg
Rate: 20 DEG/MIN TO 525/ASH
Program: TGA Analysis V1.0

TGA

Date: 5-Nov-84 Time: 15:00:31
File: UVIC.18 MISC TEST XI
Operator: ERIN
Plotted: 6-Nov-84 7:54:34

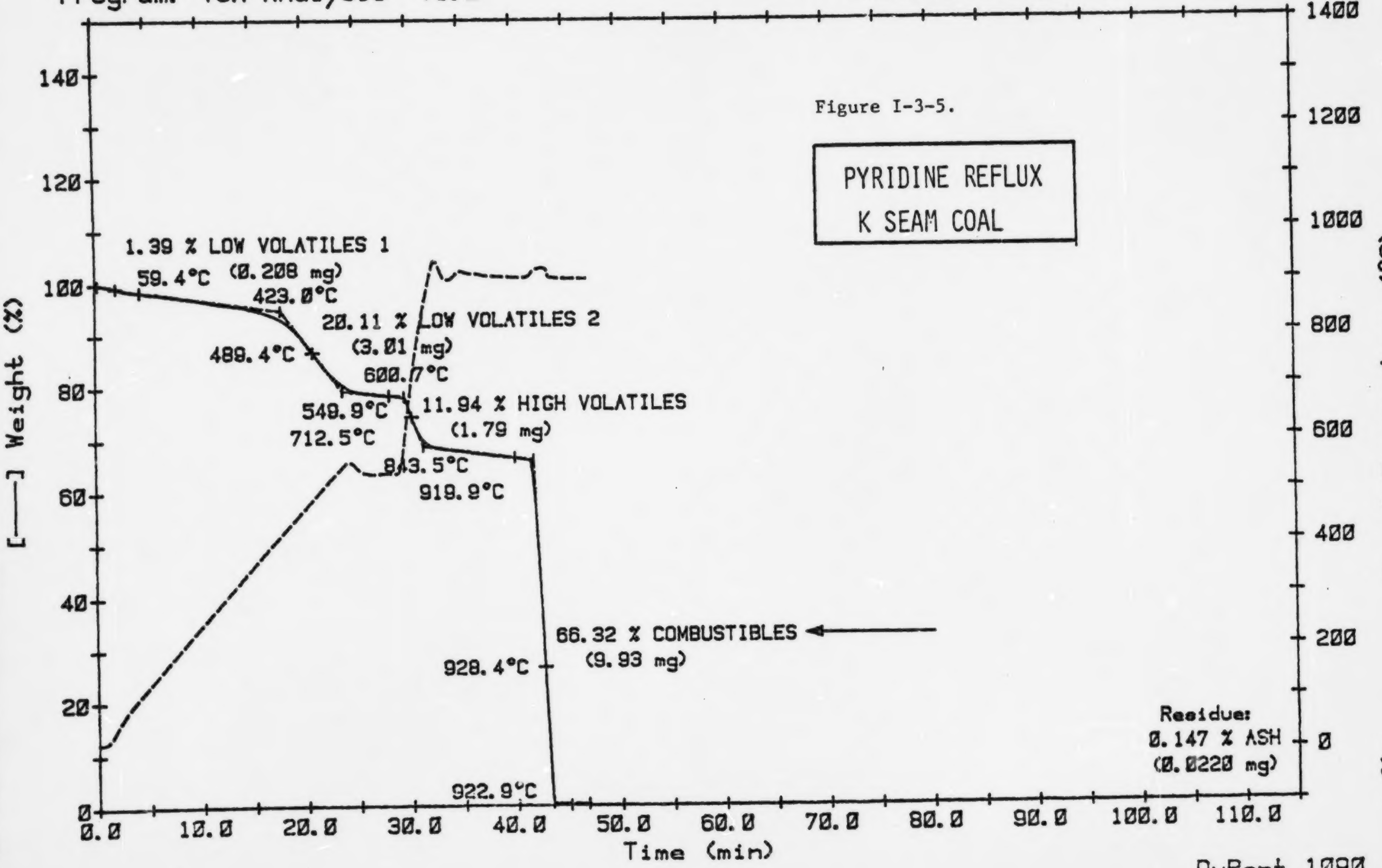


Figure I-3-5.

Sample: U.VIC 2-49C
Size: 22.61 mg
Rate: 20 DEG/MIN TO 525/ASH
Program: TGA Analysis V1.0

TGA

Date: 11-Oct-84 Time: 13:26:05
File: UVIC.11 MISC TEST X
Operator: ERIN
Plotted: 11-Oct-84 14:57:22

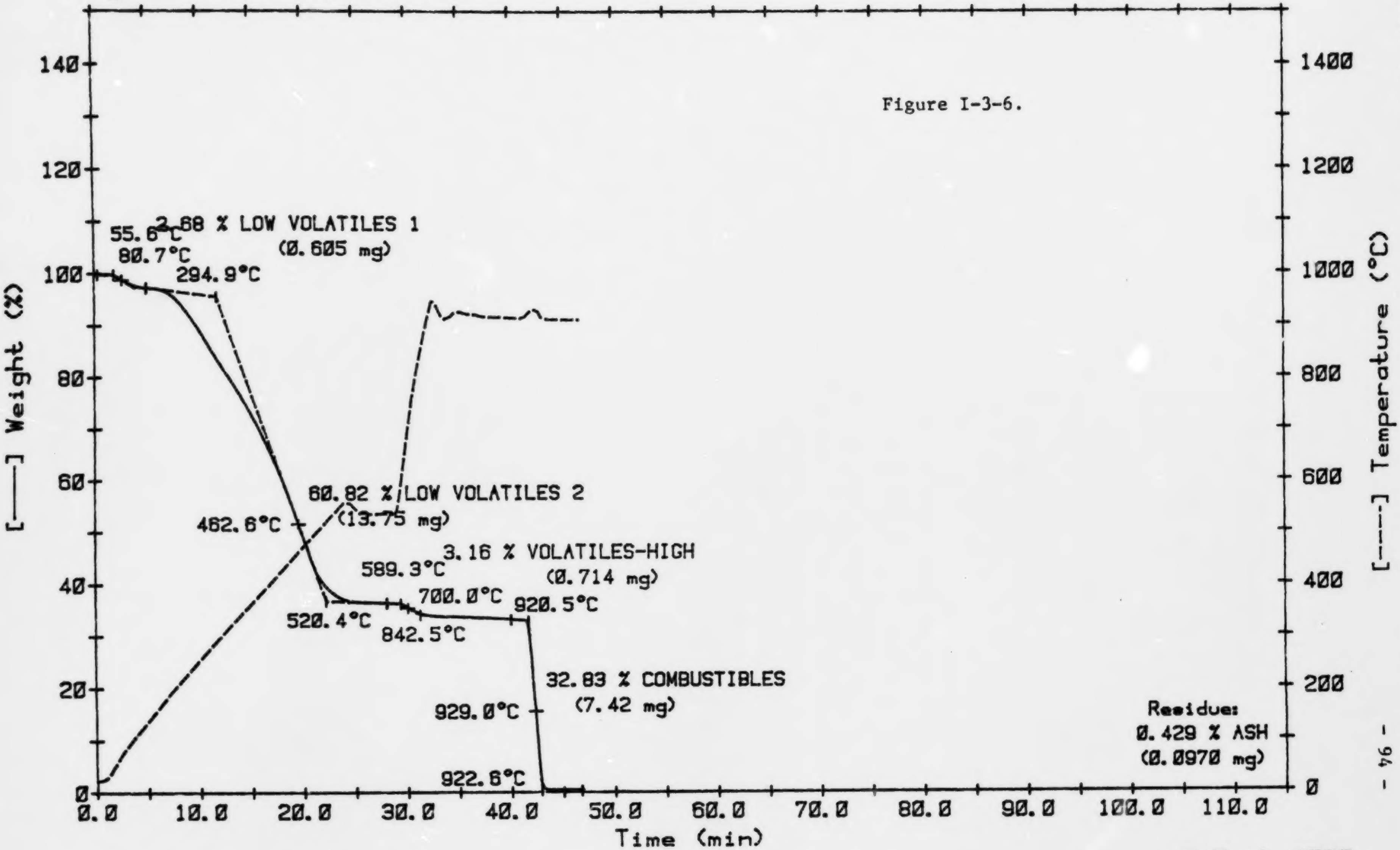


Figure I-3-6.

DuPont 1090

Sample: U.VIC 10-18C
Size: 12.36 mg
Rate: 20 DEG/MIN TO 525/ASH
Program: TGA Analysis V1.0

TGA

Date: 18-Oct-84 Time: 13:34:18
File: UVIC.15 MISC TEST X
Operator: ERIN
Plotted: 18-Oct-84 15:10:40

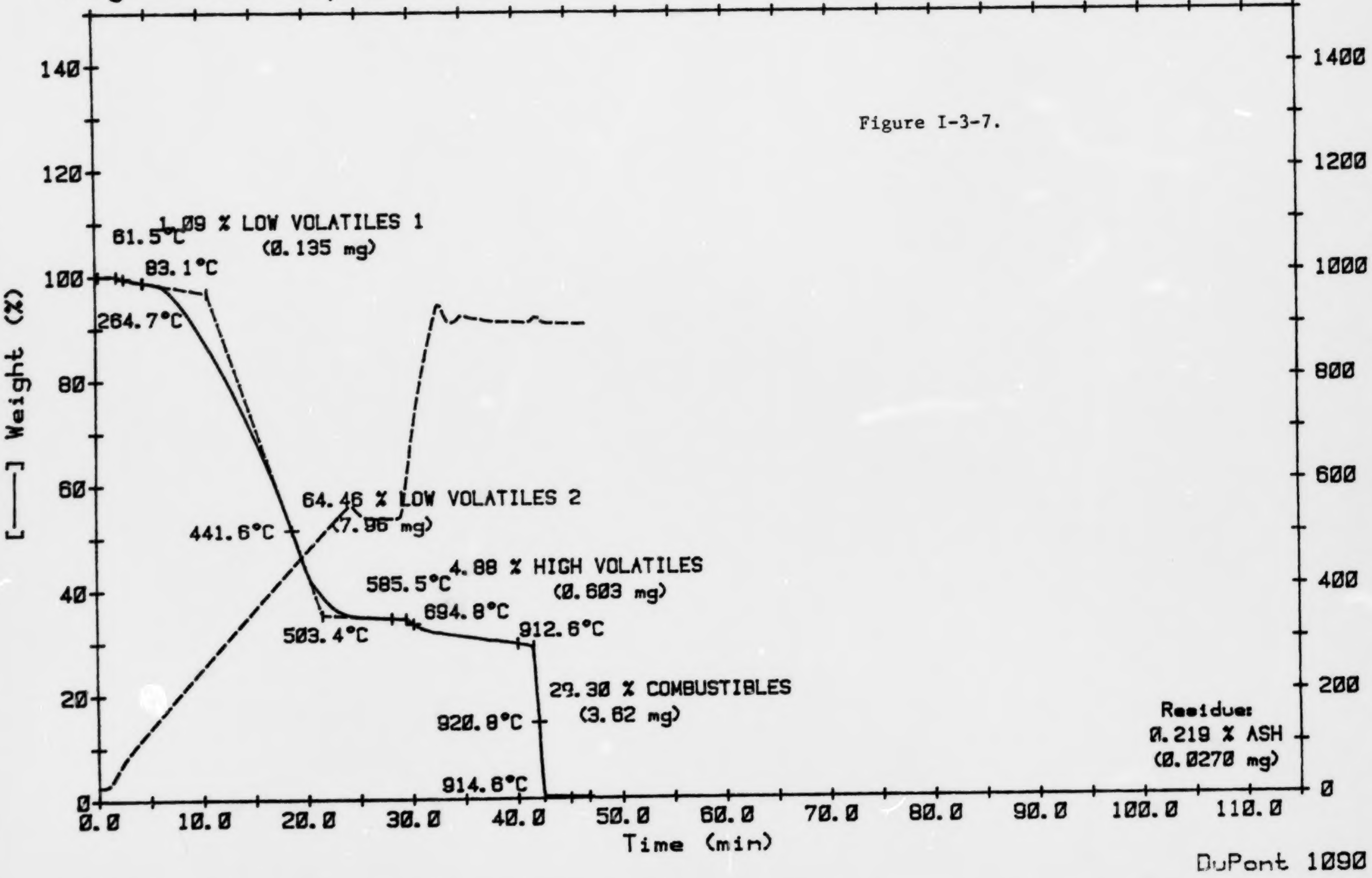


Figure I-3-7.

APPENDIX I-4
TABLE I-4-1.

General Testing Laboratories
A Division of SGS Supervision Services Inc.
1001 East Pender Street,
Vancouver, B.C. Canada V6A 1W2
Telephone: (604) 254-1647 Telex: 04-507514 Cable: Supervise

CERTIFICATE OF ANALYSIS

TO:
UNIVERSITY OF VICTORIA
P.O. Box 1700
Victoria, B.C. Canada
V8W 2Y2

CHEMISTRY DEPARTMENT

No.
FILE: 8405-1757
DATE: May 28, 1984

WE HAVE ANALYZED the herein described samples submitted by you on May 17, 1984 and report as follows:

DESCRIPTION: Nine (9) submitted Coal samples, marked as shown below:

PURCHASE ORDER NUMBER 95350
Requisition Number 60831
A/C Number 3 49594 645

ANALYSIS:	Basis	Residual Moisture	CARBON	HYDROGEN
CANMORE ANTHRACITE	Air Dry	1.07%	86.64%	3.62%
	Dry	——	87.58%	3.54%
DEVCO	Air Dry	1.38%	75.57%	5.21%
	Dry	——	76.63%	5.13%
GRANBY	Air Dry	1.95%	27.25%	2.32%
	Dry	——	27.79%	2.14%
ILLINOIS # 6	Air Dry	1.43%	66.77%	4.65%
	Dry	——	67.74%	4.56%
→ K B AIR	Air Dry	1.32%	81.38%	5.07%
	Dry	——	82.47%	4.99%
MERRIT ol-1 100 MESH	Air Dry	1.67%	63.70%	4.51%
	Dry	——	64.78%	4.40%
MARY L	Air Dry	0.82%	68.82%	4.63%
	Dry	——	69.39%	4.58%
QUINSAM	Air Dry	1.06%	70.73%	4.82%
	Dry	——	71.49%	4.75%
TELKWA 01-1 100 MESH	Air Dry	1.88%	69.05%	4.82%
	Dry	——	70.37%	4.70%

REMARKS:
Hydrogen on Air Dry Basis include Moisture

Bie Ong

Bie Ong, for
L. Lakosil, Chief Coal Chemist.
SIGNATURE AND TITLE

THIS COMPANY ACCEPTS NO RESPONSIBILITY EXCEPT FOR THE DUE PERFORMANCE OF INSPECTION AND/OR ANALYSIS IN GOOD FAITH AND ACCORDING TO THE RULES OF THE TRADE AND OF SCIENCE

Analytical and Consulting Chemists, Bulk Cargo Specialists, Surveyors, Inspectors, Samplers, Weighers
MEMBER American Society For Testing Materials - The American Oil Chemists Society - Canadian Testing Association
REFEREE AND OR OFFICIAL CHEMISTS FOR - National Institute of Oilseed Products - The American Oil Chemists Society
OFFICIAL WEIGHMASTERS FOR Vancouver Board of Trade

APPENDIX I-4
Table I-4-2.
Elemental Analysis of Coal Liquefaction Product and Residues.

Sulphur

Code No.	Analyst No.	Description	% S
2-51B AWCP Soluble	C883	K-seam B Pyridine Soluble	0.58
2-51B AWCP Insoluble	C884	K-seam Coal Residue	0.55
2-51C AWCP Soluble	C885	K-seam Clathrate Pyridine Soluble	0.55
Raw Coal K-seam By X-ray Fluorescence, per Dr. W. M. Johnson			0.45 0.75
10-38B HCl Pptd. CP Soluble	C889	Devco B fraction Pyridine Soluble	0.62
10-38B AWCP Insoluble	C890	Devco Coal Residue	1.41
10-38C HCl Pptd. CP Soluble	C891	Devco Clathrate Pyridine Soluble	0.62
Raw Coal Devco			1.69
11-10-9 HCl Pptd. Pyridine Soluble	C895	Devco Pyridine Reflux	0.54
11-2-11 Pyridine Soluble	C897	K-seam Pyridine Reflux	0.60

AWCP = Acid Washed Cold Pyridine Soluble.

APPENDIX I-4

Table I-4-3.

Elemental Analysis of Coal Liquefaction Product and Residues.

Carbon and Hydrogen

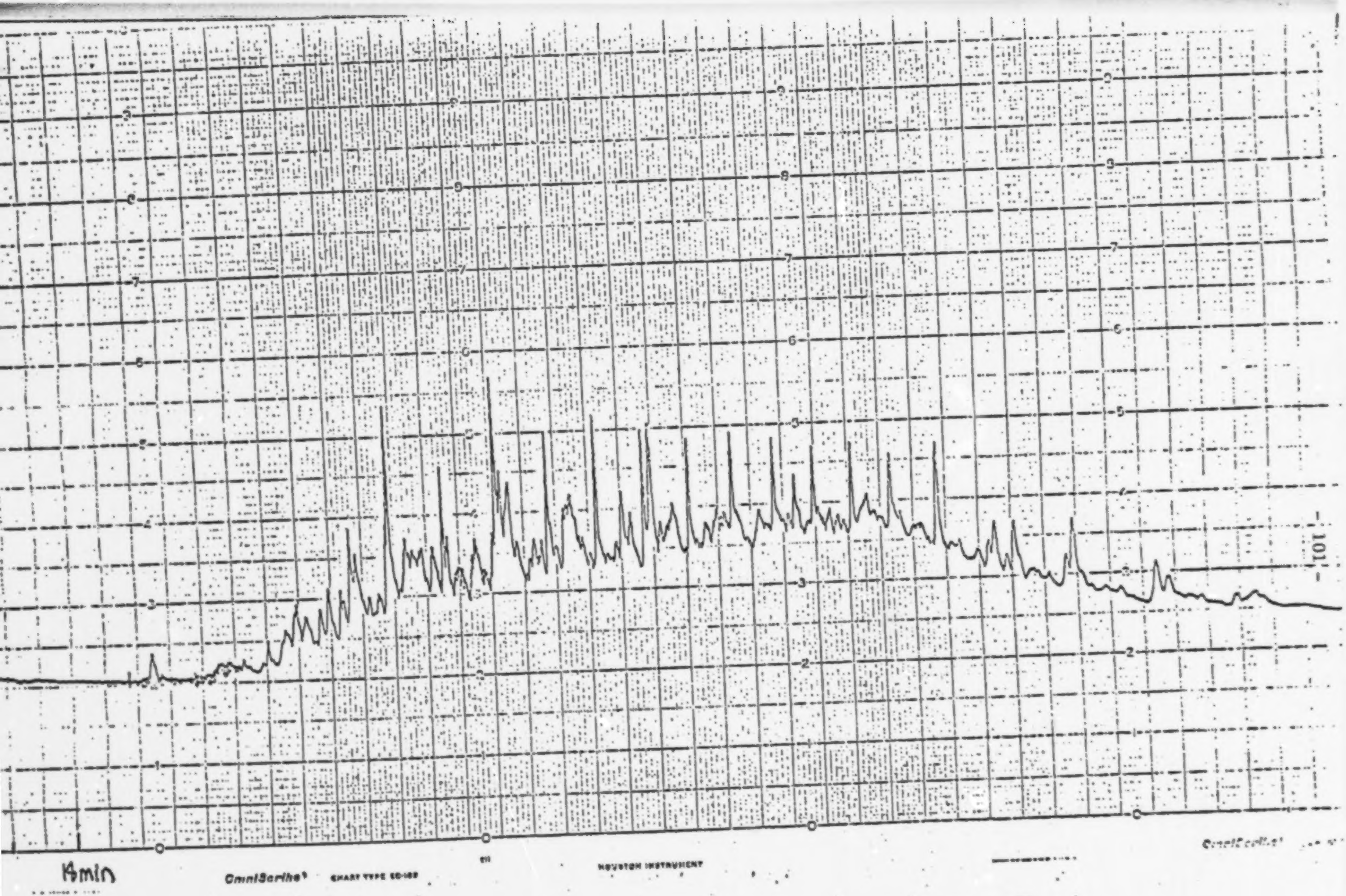
Code No.	Analyst No.	% C	% H	Description
Forestburg Raw Coal	C882	62.16	4.00	Coal sample
2-51B AWCP Sol.	C883	79.14	6.47	K-seam B, Pyridine soluble (dist., acid washed)
2-51B AWCP Insol.	C884	77.83	4.92	K-seam coal residue
2-51C AWCP Sol.	C885	78.36	5.75	K-seam clathrate, Pyridine soluble
2-51C AWCP Insol.	C886	78.18	5.08	K-seam clathrate residue (coal fines)
10-38B CENT HCl ppted. Cp Sol.	C887	82.76	5.91	Devco solid centrifuged from clathrate, Pyridine solubles
10-38B CENT AWCP Insol.	C888	78.06	5.17	Devco solid centrifuged from clathrate (coal fines)
10-38B HCl Ppted. Cp Sol.	C889	82.80	6.00	Devco B residue, Pyridine soluble
10-38B AWCP Insol.	C890	76.43	5.20	Devco coal residue
10-38C HCl Ppted. Cp Sol.	C891	80.19	5.31	Devco clathrate, Pyridine soluble
10-38C AWCP Insol.	C892	75.02	4.95	Clathrate residue, Pyridine insoluble
11-7-1 HCl Ppted. PYR Sol.	C893	79.40	7.33	Pyridine reflux Merritt, Pyridine solubles
11-7-1 AW PYR Insol.	C894	59.84	4.30	Pyridine reflux Merritt, Pyridine insoluble coal residue

APPENDIX I-4, Table I-4-3 continued

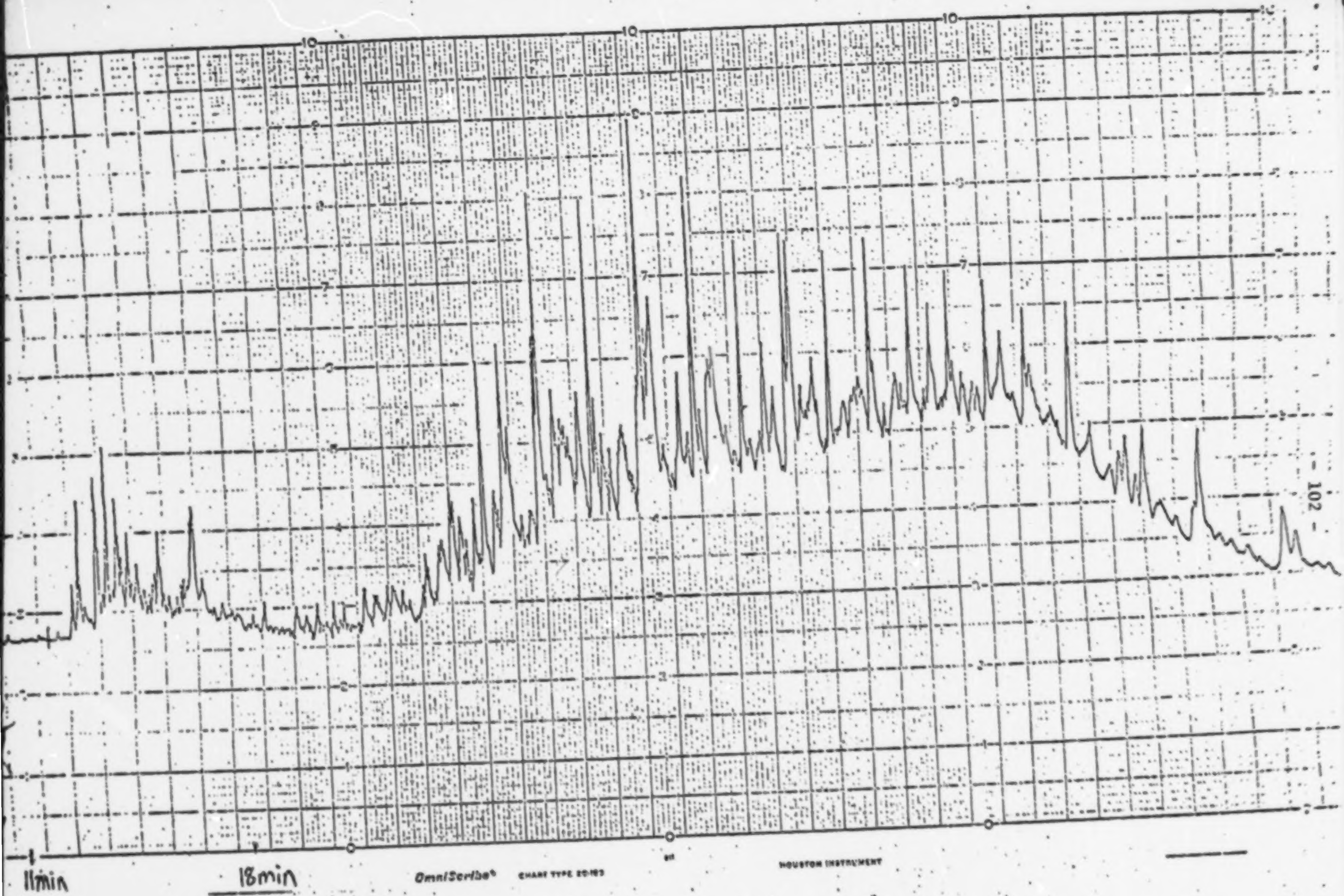
Code No.	Analyst No.	% C	% H	Description
11-10-9 HCl Ppted. PYR Sol.	C895	82.97	5.79	Pyridine reflux Devco solubles
11-10-9 AW PYR Insol.	C896	77.52	4.92	Pyridine reflux Devco coal residue
11-2-11 PYR Sol.	C897	82.58	5.76	Pyridine reflux K-seam solubles
11-2-11 AW PYR Insol.	C898	77.73	4.78	Pyridine reflux K-seam coal residue
11-14-3 PYR Sol.	C899	83.65	5.68	Pyridine reflux Mary Lee solubles
11-14-3 PYR Insol.	C900	64.29	4.19	Pyridine reflux Mary Lee coal residue
11-16-1 HCl Ppted. PYR Sol.	C901	87.76	5.52	Pyridine reflux Balmer high volatile solubles
11-16-1 AW PYR Insol.	C902	78.36	3.91	Pyridine reflux Balmer high volatile coal residue
11-19-1 HCl Ppted. PYR Sol.	C903	87.55	5.62	Pyridine reflux Balmer low volatile solubles
11-19-1 AW PYR Insol.	C904	77.76	4.09	Pyridine reflux Balmer low volatile insolubles
16-4B AWCP Insol.	C906	77.95	3.99	Balmer high volatile coal residue (pyridine insolubles)
16-4C HCl Ppted. Cp Sol.	C907	82.46	5.05	Balmer high volatile clathrate pyridine solubles
16-4C AWCP Insol.	C908	81.70	4.71	Balmer high volatile clathrate insolubles (coal fines)
19-1B HCl Ppted. Cp Sol.	C909	84.12	5.65	Balmer low volatile B residue pyridine solubles

APPENDIX I-4, Table I-4-3 (continued).

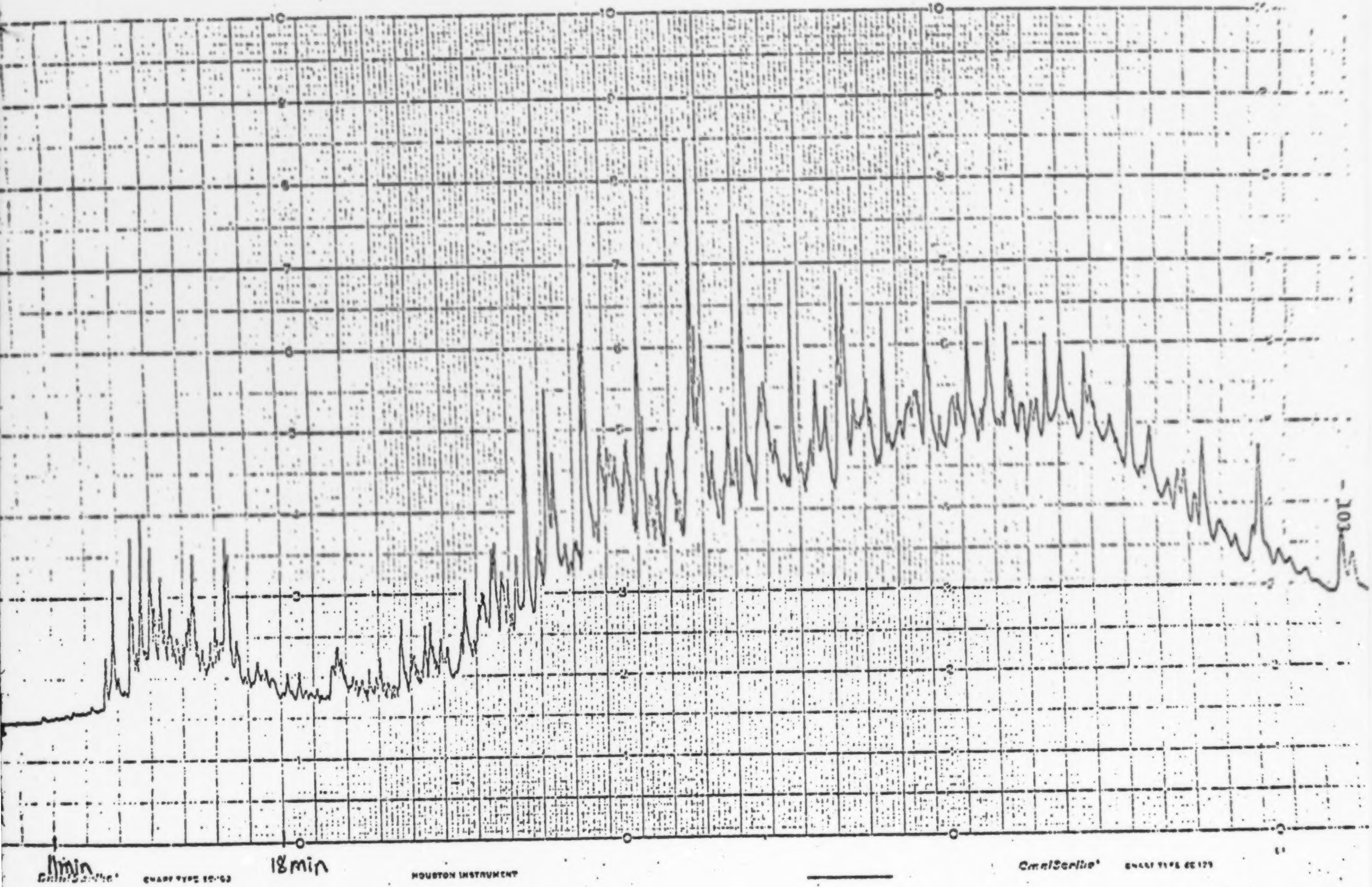
Code No.	Analyst No.	% C	% H	Description
19-1B AWCP Insol.	C910	77.02	4.30	Balmer low volatile coal residue
19-1C HCl Ppted. Cp Sol.	C911	84.86	5.34	Balmer low volatile clathrate soluble
19-1C AWCP Insol.	C912	81.62	4.76	Balmer low volatile clathrate residue (coal fines)
11-21-1 HCl Ppted. PYR Sol.	C913	73.76	7.59	Forestburg pyridine reflux solubles
11-21-1 AW PYR Insol.	C914	64.46	4.33	Forestburg pyridine reflux coal residue



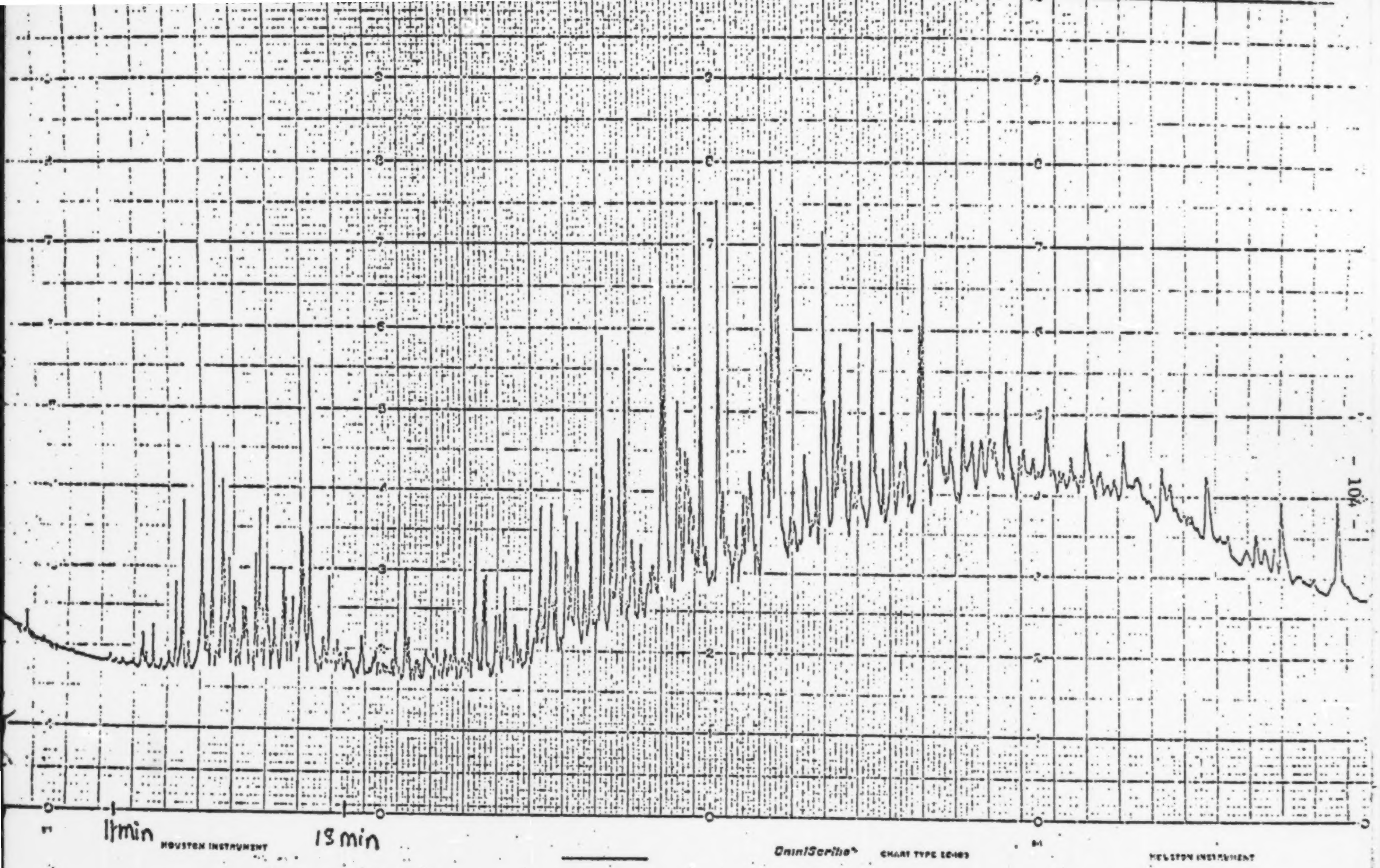
Sample 11-2-2-4
Toluene soluble material produced by clathrate extraction of K-seam coal ("as is").



Sample 11-2-2-3.
Toluene soluble material produced by clathrate extraction of K-seam coal
(after Sep-pak cleaning with methylene chloride).



Sample 11-2-2-2.
Toluene soluble material produced by clathrate extraction of K-seam coal
(after Sep-pak cleaning with 25% methylene chloride/75% pentane).



Sample 11-2-2-1
Toluene soluble material produced by clathrate extraction of K-seam coal
(after Sep-pak cleaning with pentane).

APPENDIX I-5

GC/MS Analysis Toluene Solubles K-seam Extract

PRELIMINARY EVALUATION

Table I-5-1. Pentane elution from Sep-Pak

Relative Retention Index (RRI)/CI	Molecular Weight	R.R.I. from E.I.	Possible Identity
200.0	128	200.0	Naphthalene (standard)
220.7	142	220.4	2-Methylnaphthalene
222.5	184	222.2	$C_{13}H_{28}$-branched hydrocarbon
223.6	142	223.5	1-Methylnaphthalene
233.9	198	-	$C_{14}H_{30}$-branched hydrocarbon
236.1	154	236.0	Biphenyl
238.5	156	238.2	1 or 2-Ethylnaphthalene
239.1	156	-	2,6-Dimethylnaphthalene
240.3	156	240.0	2,7-Dimethylnaphthalene
242.0	212	-	$C_{15}H_{32}$-branched hydrocarbon
242.8	156	242.8	1,3 or 1,7-Dimethylnaphthalene
243.5	156	243.7	1,6-Dimethylnaphthalene
245.8	156	245.6	2,3-Dimethylnaphthalene + another component
246.3	156	246.2	1,4-Dimethylnaphthalene
246.8	156	246.6	1,5-Dimethylnaphthalene
248.8	156	248.6	1,2-Dimethylnaphthalene
251.1	226	-	$C_{16}H_{34}$-branched hydrocarbon
254.5	168/170	254.4	mixtures possibly containing methylbiphenyls
256.1	168/170	255.8	
257.5	170	257.3	Iso-propylnaphthalene (?)
259.0	168	258.8	Dibenzofuran
260.4	170	260.1	a Methyl-ethylnaphthalene (?)
261.1	170	260.8	a Methyl-ethylnaphthalene (?)
261.8	170	261.7	a Methyl-ethylnaphthalene (?)
264.3	170	264.0	2,3,6-Trimethylnaphthalene (?)
266.4	240	-	$C_{17}H_{36}$-branched hydrocarbon
267.1	170	267.0	2,3,5-Trimethylnaphthalene
269.9	170	269.4	a Trimethylnaphthalene
271.0	170	270.8	a Trimethylnaphthalene
272.1	182	-	

Table I-5-1 continued.

Relative Retention Index (RRI)/CI	Molecular Weight	R.R.I. from E.I.	Possible Identity
272.9	Mixture	272.5	Mixture
273.8		273.5	Mixture (possibly containing a phthalate)
276.3	182	275.8	4,4'-Dimethylbiphenyl (?)
277.4	184	277.2	a 'C_4'-substituted naphthalene
278.2	182	277.8	3,3'-Dimethylbiphenyl (?)
279.9	182	279.3	2,2'-Dimethylbiphenyl (?)
280.9	184	280.6	1-Methyl,7-isopropylnaphthalene (?)
281.7	254	281.5	$C_{18}H_{38}$-branched hydrocarbon
283.4	254	-	$C_{18}H_{38}$-branched hydrocarbon
284.2	184	283.8	a 'C_4'-substituted naphthalene
286.3	184	-	a 'C_4'-substituted naphthalene
286.7			
287.3	184	-	a 'C_4'-substituted naphthalene
289.1	180	288.6	1 or 2-Methylfluorene
289.8	240	289.6	$C_{17}H_{36}$ (?)
290.6	268	290.4	$C_{19}H_{40}$-branched hydrocarbon
293.7	196	293.3	Isomers as yet unidentified
294.7	196	294.5	
295.7	196	295.8	
296.8	196	296.5	
297.5	196	-	
299.0	196	-	
300.0	178	300.0	Phenanthrene (standard)
301.5	178	301.5	Anthracene (standard)
302.9	270	-	
305.5	254	305.3	$C_{18}H_{38}$ (?)
313.1	210	312.9	
314.0	210	-	
317.4	210,242	317.3	Mixture
319.3	192	319.0	3-Methylanthracene
320.3	192	320.0	2-Methylphenanthrene
321.8	192 and 268	321.9	a Methylphenanthrene and $C_{19}H_{40}$ (?)

Table I-5-1 continued.

Relative Retention Index (RRI)/CI	Molecular Weight	R.R.I. from E.I.	Possible Identity
323.2	192	322.9	1-Methylanthracene or 4- or 9-methylphenanthrene
324.2	192	324.0	1-Methylphenanthrene
332.1	204	331.8	Possibly a phenylnaphthalene
333.5	256(?)	334.2	
336.9	206		(9-)Ethylphenanthrene
337.7	282		$C_{20}H_{42}$-branched hydrocarbon
341.1	206	341.1	(2,7)-Dimethylphenanthrene
342.4	206	342.3)	'C_2'-substituted phenanthrenes or anthracenes
343.2	206	342.9)	
344.2	206	)	
344.7	206	344.7)	
346.5	206	346.5)	
348.9	206 and 220	348.7	Mixture
353.1	282	353.2	$C_{20}H_{42}$-Isomer
359.0	220	358.9	a 'C_3'-substituted phenanthrene
361.0	220	-	9-Methyl, 10-ethylphenanthrene
361.8	220	-	a 'C_3'-substituted phenanthrene
362.9	282	-	$C_{20}H_{42}$-Isomer
366.5	216 and 220	-	216 = Benzo[a]fluorene
367.1	282	367.0	$C_{20}H_{42}$
368.2	234	368.2	a 'C_4'-substituted phenanthrene
369.7	282	-	$C_{20}H_{42}$
371.8	232	372.0	
373.4	282(?)	373.2	$C_{20}H_{42}$(?)
374.2	232	374.2	
381.1	282	381.3	$C_{20}H_{42}$
383.4	230(?)	-)	Isomers unidentified
384.1	230(?)	-)	
386.5	230(?)	-)	
388.1	278	387.9	Dibutylphthalate
388.9	230(?)	-	
394.1	246	394.4	
400.0	228	400.0	Chrysene (standard)

APPENDIX I-5.

Table I-5-2. Methylene Chloride elution from Sep-Pak

PRELIMINARY EVALUATION

R.R.I. from C.I.	Molecular Weight	R.R.I. from E.I.	Possible Identity
200.0	128	200.0	Napthalene (standard)
203.9	170	-	$C_{12}H_{26}$
220.8	142	220.4	2-Methylnaphthalene
222.7	184	-	$C_{13}H_{28}$
223.8	142	223.4	1-Methylnaphthalene
236.5	154	-	Biphenyl
238.9	156	-	1- or 2-Ethylnaphthalene
239.5	156	-	2,6-Dimethylnaphthalene
240.7	156	240.4	2,7-Dimethylnaphthalene
243.2	156	243.0	1,3 or 1,7-Dimethylnaphthalene
243.9	156	243.7	1,6-Dimethylnaphthalene
246.1	156	-	2,3-Dimethylnaphthalene + another component
246.7	156	246.3	1,4-Dimethylnaphthalene
247.2	156	-	1,5-Dimethylnaphthalene
249.2	156	248.9	1,2-Dimethylnaphthalene
250.7	226(?)	-	$C_{16}H_{32}$
254.7	168	254.8	a Methylbiphenyl
256.3	168	-	a Methylbiphenyl
257.8	170	257.6	Iso-propylnaphthalene (?)
259.6	168	259.3	Dibenzofuran
260.6	170	260.6	a Methylethylnaphthalene (?)
261.3	170	261.3	a 'C_3'-substituted naphthalene
262.1	170	261.8	a 'C_3'-substituted naphthalene
263.2	172	263.1	
264.8	170	264.5	2,3,6-Trimethylnaphthalene
266.4	240(?)	-	$C_{17}H_{36}$
267.4	170	267.2	2,3,5-Trimethylnaphthalene
270.1	170	-	a Trimethylnaphthalene
270.8	200	-	
271.3	170	271.0	a Trimethylnaphthalene
272.3	182	-	
273.9	182	-	

APPENDIX I-5.

Table I-5-2. continued.

R.R.I. from C.I.	Molecular Weight	R.R.I. from E.I.	Possible Identity
274.5		274.1	Possibly a phthalate
276.6	182	276.5	4,4'-Dimethylbiphenyl
278.4	182	278.4	3,3'-Dimethylbiphenyl
279.9	184 + another	280.0	a 'C_4'-substituted naphthalene + another component
281.9	254	-	$C_{18}H_{38}$
283.4	254	-	$C_{18}H_{38}$
284.4	184	284.4	a 'C_4'-substituted naphthalene
286.8	184	-	a 'C_4'-substituted naphthalene
387.3	184	-	a 'C_4'-substituted naphthalene
289.6	240	289.4	$C_{17}H_{36}$
290.5	268	290.1	$C_{19}H_{40}$
292.9	?	292.9	
293.9	196	293.8)	
294.7	196	294.8)	
295.8	196	-)	Isomers as yet unidentified
296.7	196	296.9)	
297.4	196	-)	
299.2	196	-)	
300.0	178	300.0	Phenanthrene (standard)
301.3	178	301.7	Anthracene (standard)
303.3	270	303.5	
305.4	254	305.8	$C_{18}H_{38}$
313.1	210 and 242(?)	-	
314.1	210	-	
317.2	242	-	
319.2	192	319.4	3-Methylphenanthrene
320.3	192	320.2	2-Methylphenanthrene
321.8	268 and 192	-	$C_{19}H_{40}$ and a Methylphenanthrene
322.9	192 and 282	322.5	
330.2	282(?)	-	$C_{20}H_{42}$ (?)
333.7	256(?)	-	
336.8	206	-	An ethylphenanthrene

APPENDIX I-5.
Table I-5-2 continued.

R.R.I. from C.I.	Molecular Weight	R.R.I. from E.I.	Possible Identity
337.8	282	338.3(?)	$C_{20}H_{42}$
341.2	206	341.3	2,7-Dimethylphenanthrene
341.9	206	-)	'C_2'-substituted phenanthrenes
342.9	206	-)	
344.5	206	-)	
348.4	270(?)	-	
359.1	220	-	a 'C_3'-substituted phenanthrene
359.9	282	-	$C_{20}H_{42}$
361.4	220 and 282	-	a 'C_3'-substituted phenanthrene + $C_{20}H_{42}$
363.5	282	-	$C_{20}H_{42}$
366.6	216 and 220		216-Benzo[a]fluorene
367.4	?	-	
	234	368.0	a 'C_4'-substituted phenanthrene (?)
371.7	232	-	
374.0	232	-	
386.6	280 (?)	-	
388.3		388.3	Dibutylphthalate
390.8	282 (?)	-	
400.0	228	400.0	Chrysene (standard)

APPENDIX I-5.

Table I-5-3. Gc/ms Pentane Soluble Sep-pak Separation
K-seam Toluene Reflux
Sample 11-2-0-1-1

Peak No.	Rel. Ret. Index	m/e		M.W.	Identity
		CI	EI		
1	200.0	129	128	128	Naphthalene
2					
3					
4					
5					
6	220.39	143		142	2-Methylnaphthalene
7	222.47	183		184	$C_{13}H_{28}$ Branched
8	223.44	143		142	1-Methylnaphthalene
9	236.20	155		154	Biphenyl
10	238.56	157		156	1 or 2-Ethylnaphthalene
11	239.11	157		156	2,6-Dimethylnaphthalene
12	240.22	157		156	2,7-Dimethylnaphthalene
13	242.86	157		156	1,3,1,7 or 1,6-Dimethylnaphthalene
14	246.33	157		156	2,3 or 1,4-Dimethylnaphthalene
15	248.96	157		156	1,2-Dimethylnaphthalene (2,2-bipyridyl)
16	251.46	225		226	$C_{16}H_{34}$
17	254.79	169		168/170	Methylbiphenyl (168)
18	256.31	169		168/170	"
19	257.28	171		170	
20	257.70	171		170	iPr naphthalene iPr = i-propyl
21	259.23	169		168	Dibenzofuran
22	260.47	171		170	Methylethylnaphthalene
23	261.3	171		170	Methylethylnaphthalene
24	262.0	171		170	Methylethylnaphthalene
25	264.2	171		170	Methylethylnaphthalene
26	264.6	171		170	2,3,6-Trimethylnaphthalene
27	266.7	171		170	Trimethylnaphthalene
28	267.3	171		170	2,3,5-Trimethylnaphthalene
29	270.0	171,167, 185		170 (166,184)	Fluorene (166) Dibenzodioxin (184)
30	271.0	171		170	Trimethylnaphthalene isomer
31	272.4	183		182	3,3'-dimethylbiphenyl
32	273.2	185		184	Unassigned, 4-C substituted naphthalene

APPENDIX I-5.
Table I-5-3 continued.

Peak No.	Rel. Ret. Index	m/e CI	m/e EI	M.W.	Identity
33	274.1	183/171		182/170	C-2 Biphenyl (182)
34	274.5	--		--	No molecular ion
35	276.0	185		184	4-C Naphthalene
36	276.4	183		182	4,4'-Dimethylbiphenyl
37	277.7	185		184	4-C Naphthalene
38	278.5	183		182	3,3'-Dimethylbiphenyl
39	280.0	183/185		182/184	2,2'-Dimethylbiphenyl (182)
40	280.9	185		200/184	2-Methyl-isopropyl-naphthalene (184)
41	282.0	185/253		184/254	$C_{18}H_{38}$ (254), 4-C Naphthalene
42	283.6	185		184	4-C Naphthalene
43	284.5	--		--	No molecular ion
44	286.1	--		--	No molecular ion
45	286.7	185		184	4-C Naphthalene
46	287.5	185		184	4-C Naphthalene
47	288.4	185,181 197		<184,180, 196>	2-Methylfluorene (180)
48	289.3	181,197		<180,196>	1-Methylfluorene
49	290.2	197/185 239		<196,184, 240>	$C_{17}H_{36}$ normal alkane
50	291.0	267,183		<182,268>	$C_{19}H_{40}$ branched
51	293.5	185,183		184/182	
52	294.0	185,197		196/184	Dibenzothiophene
53	294.9	197		196	Trimethylbiphenyl or
54	296.1	197		196	Methylethylbiphenyl
55	296.8	197		196	"
56	297.8	197		196	"
57	299.2	197		196	"
58	300.0	179		178	Phenanthrene standard
59	301.7	179		178	Anthracene standard
60	303.1	269		?	Unidentified
61	305.4	253		254	π-$C_{18}H_{38}$
62	307.1	195		194	Methyldihydrophenanthrene (194)
63	307.7	211/195		210/194	"
64	309.8	211		210	Dimethylethylbiphenyl (210)
65	310.4	211/195		210/194	or
66	312.4	211		210	Tetramethylbiphenyl (210)

APPENDIX I-5.
Table I-5-3 continued.

Peak No.	Rel. Ret. Index	m/e		M.W.	Identity
		CI	EI		
67	313.5	211		210	Tetramethylbiphenyl (210)
68	314.6	211		210	"
69	316.5	211		210	"
70	317.8	193/211		192/210	"
71	318.4	193		192	2-Methylphenanthrene
72	319.1	193		192	3-Methylphenanthrene
73	320.2	211		210	Tetramethylbiphenyl
74	321.1	267		268	η-$C_{19}H_{40}$
75	321.9	193		192	2-Methylanthracene
76	322.8	193		192	1-Methylanthracene
77	325.4	--		--	No molecular ion
78	330.2	205		204	4,5-Dihydropyrene
79	332.9	Frag.235		(206)	Unidentified
80	334.9	Frag.235		--	No molecular ion
81	336.6	207,281		206/282	2 or 9-Ethylphenanthrene, $C_{20}H_{42}$
82	337.2	207		206	Dimethylphenanthrene
83	338.1	207		206	2 or 9-Ethylphenanthrene
84	339.4	207		206	3,6-Dimethylphenanthrene
85	340.1	Frag.235			Isomer of 87
86	341.0	207		206	2,7-Dimethylphenanthrene
87	342.1	Frag.235			Isomer of 85
88	342.9	207		206	C-2 Phenanthrene or anthracene
89	344.6	207		206	C-2 phenanthrene or anthracene
90	346.9	207		206	1,8-Dimethylphenanthrene
91	349.8	203		202	Tetracyclic (pyrene or isomer) (202)
92	351.2	--		--	Unidentified, no molecular ion
93	351.8	219		218	Methyl substituted dihydropyrene (218)
94	354.1	219		218	"
95	356.1	221		220	Trimethyl- Ethyl- or Propyl- Phenanthrenes or Anthracenes (220)
96	356.7	221		220	
97	358.7	221		220	
98	359.4	221		220	"
99	362.5	221		220	"
100	363.4	221		220	"
101	364.5	221,217		220/216	Mixture, 216 Major
102	364.9	217		216	Methylpyrene
103	365.9	235		234	C-4 substituted phenanthrene or anthracene

APPENDIX I-5.
Table I-5-3 continued.

Peak No.	Rel.Ret. Index	m/e CI	m/e EI	M.W.	Identity
104	366.5	235		234	C-4 substituted phenanthrene or anthracene
105	368.0	221/217		220/216	C-3 anthracene (220), methylpyrene (216)
106	369.8	233		232	Dimethyldihydropyrene
107	371.8	233		232	"
108	382.4	231		230	Dimethylpyrene
109	387.3	231		230	"
		235		234	C-4 anthracene
110					Chrysene

APPENDIX I-5.

Table I-5-4. Gc/ms Pentane Soluble Sep-Pak Separation
Toluene Layer Clathrate (A)
K-seam
Sample 2-56-11

Peak No.	Rel. Ret. Index	m/e CI	m/e EI	M.W.	Identity
1	141.9	✓		--	No molecular ion
2	144.4	✓		--	Fragments only
3	149.3	✓		--	" "
4	156.6	✓		--	" "
5	172.2	✓		--	" "
6	173.6	✓		--	" "
7	177.0	✓		--	" "
8	178.8	✓		--	" "
9	180.7	✓		--	" "
10	182.7	✓		--	" "
11	185.3	155		156	$\pi C_{11}H_{24}$
12	188.0	135		134	Background (low intensity)
13	188.8	135		134	"
14	189.7	--		--	Fragments only
15	194.8	--		--	" "
16	195.7	--		--	" "
17	196.1	133		132	Tetralin
18	197.1	--		--	Fragments only
19	197.8	--		--	" "
20	200.0	--		128	Naphthalene standard
21	203.8	169		170	$\pi C_{12}H_{26}$
22	204.3	157 (138)		156 (137)	Unidentified
23	205.9	138 (157)		137 (156)	Unidentified
24	211.2	158,160		--	No molecular ion
25	212.7	158,160		--	" " "
26	214.5	--		--	" " "
27	217.0	--		--	" " "
28	219.3	159		158	Unidentified
29	220.4	143		142	2-Methylnaphthalene
30	222.5	183		184	$C_{13}H_{28}$(branched)
31	223.5	143		142	1-Methylnaphthalene
32	225.1	--		--	Low intensity (background)
33	229.2	--		--	" "
34	229.8	--		--	" "
35	231.2	--		--	" "

APPENDIX I-5.

Table I-5-4 continued.

	Rel. Ret.	m/e			
Peak No.	Index	CI	EI	M.W.	Identity
36	233.1	(197)		(198)	Minor
37	233.9	197		198	$\eta C_{14}H_{30}$
38	236.2	155		154	Biphenyl
39	238.6	157		156	1- or 2-Ethylnaphthalene
40	239.1	157		156	2,6-Dimethylnaphthalene
41	240.4	157		156	2,7-Dimethylnaphthalene
42	242.9	157		156	1,3,1,7,1,6-Dimethylnaphthalene (Major)
43	246.2	157		156	2,3- or 1,4-Dimethylnaphthalene
44	248.2	--		--	Background
45	248.9	157		156	1,2-Dimethylnaphthalene
46	251.0	163		162	Unidentified
47	251.5	225		226	$C_{16}H_{34}$ (branched)
48	252.8*	201		200	Unidentified
49	254.8	169(171)		168(170)	Methylbiphenyl
50	255.9*	201		200	Unidentified
51	256.4	169(171)		168(170)	3- or 4-Methylbiphenyl
52	257.3	171(211)		170,212	Mixture
53	257.8	171(211)		170,212	$\eta C_{15}H_{32}$ = 212 isopropyl naphthalene = 170
54	259.4	169		168	Dibenzofuran
55	260.8	183 (105)	Base 91	182	C-2 Biphenyl (182) Possible bibenzyl or methyldiphenylmethane
56	262.2	171		170	C-3 Naphthalene (methylethyl)
57	262.9	105(91)		--	Possible fragment of methyldiphenylmethane
58	264.3	105(91)		--	Possible fragment of methyldiphenylmethane
59	264.8	171		170	2,3,6-Trimethylnaphthalene
60	265.9	225		--	Possible 226 $C_{16}H_{34}$
61	266.8	225		--	" "
62	267.3	170		171	2,3,5-Trimethylnaphthalene
63	269.7	--		--	Minor component
64	270.3	171,167, 185,201		170,166 184,200	Mixture: Fluorene (166) C-3 Naphthalene (170)
65	271.2	171		170	C-3 Naphthalene
66	272.5	183		182	3,3'-Dimethylbiphenyl
67	273.3	177 Base		--	Unidentified

APPENDIX I-5.

Table I-5-4 continued.

	Rel. Ret.	m/e			
Peak No.	Index	CI	EI	M.W.	Identity
68	274.0	183,171, 177,201, 225		182(170)	Dimethylbiphenyl
69	275.8	185(201)		184	C-4 Naphthalene
70	276.5	183		182	4,4'-Dimethylbiphenyl
71	277.5	185		184	C-4 Naphthalene
72	278.1	183,185		184,182	C-4 Naphthalene C-2 Biphenyl
73	278.6	183		182	C-2 Biphenyl
74	280.0	201 Base		200	Unidentified
		(183)		(182)	2,2'-Dimethylbiphenyl
75	282.0	253		254	$C_{18}H_{38}$
76	283.7	--		--	Background
77	284.2	185		184	C-4 Naphthalene
78	285.9	--		--	Background
79	286.5	185,197 199		184	C-4 Naphthalene
80	287.6	185(201)		184(200)	C-4 Naphthalene
81	288.3	197		196	C-4 Naphthalene
		181		180	2-Methylfluorene
82	289.3	181		180	1-Methylfluorene
		(199)		(198)	C-5 Naphthalene
		(197)		(196)	C-3 Biphenyl
83	290.0	239		240	$\eta C_{17}H_{36}$
84	290.8	267		268	$C_{19}H_{40}$ branched
85	293.2	--		--	Background
86	293.9	197,185		196	C-3 Biphenyl Dibenzothiophene (184)
87	294.7	197		196	C-3 Biphenyl:
88	295.8	197		196	Trimethyl
89	296.5	197		196	or
90	297.5	197		196	Dimethylethyl
91	299.2	197		196	"
92	300.0	179		178	Phenanthrene standard
93	301.6	179		178	Anthracene standard
94	303.2	--		--	Baseline
95	305.6	253		254	$\eta C_{18}H_{38}$
96	307.1	195		194	Methyldihydrophenanthrene (194)
		281(201)		282	$C_{20}H_{42}$ branched (201 fragment)
97	310.3	211		210	C-4 Biphenyl
		195		194	Methyldihydrophenanthrene or anthracene
		(201)			No molecular ion possibly $C_{20}H_{42}$

APPENDIX I-5.
Table I-5-4 continued.

Peak No.	Rel. Ret. Index	m/e		M.W.	Identity
		CI	EI		
98	310.9	211		210	Overlap with 97
		195		194	
		(201)			
99	312.2	201,199			Main ion
		(211)		210	
100	313.0	211		210	C-4 Biphenyl
101	313.9	211		210	" "
102	315.0	(201)		282	Diterpene
103	317.0	(201)		282	"
		211		210	C-4 Biphenyl
104	318.9	193		192	3-Methylphenanthrene
		(211)		(210)	
105	319.9	193		192	2-Methylphenanthrene
106	321.2	193		192	C-1 Anthracene or phenanthrene
		(201)			
107	322.1	267		268	$nC_{19}H_{40}$
108	322.9	193		192	9-Methylphenanthrene or 4-Methylphenanthrene
109	323.7	193		192	1-Methylanthracene or 1-Methylphenanthrene
110	324.5	(201)		?	No molecular ion
	<suspected contamination>				
111	329.2	(201)		?	No molecular ion
112	331.6	205		204	4,5-Dihydropyrene
113	332.4	(225)		224	Unidentified
114	336.4	207		206	C-2 Phenanthrene
115	337.7	207		206	C-2 Phenanthrene
		225		224	Unidentified
		267		268	$C_{19}H_{40}$
116	339.7	207		206	3,6-Dimethylphenanthrene or 2,7-Dimethylphenanthrene or 2-Ethylphenanthrene
117	340.9	235(frag)			Unidentified
118	341.8	207		206	C-2 Phenanthrene or anthracene
119	342.6	207		206	C-2 Phenanthrene or anthracene
120	343.6	207		206	C-2 Phenanthrene or anthracene
121	344.2	207		206	C-2 Phenanthrene or anthracene
122	346.0	207		206	C-2 Phenanthrene or anthracene

APPENDIX I-5.
Table I-5-4 continued.

Peak No.	Rel. Ret. Index	m/e		M.W.	Identity
		CI	EI		
123	348.4	207		206	1,8-Dimethyl-phenanthrene
124	349.8	219		218	C-1 Dihydropyrene* or
125	351.6	219		218	
		203		202	pyrene or isomer
126	353.0	219		218	C-1 Dihydropyrene
127	355.8	219		218	" "
128	358.3	249		--	Unidentified
		273		--	"
129	360.4	221		220	C-3 Phenanthrene
130	361.2	221		220	" "
131	366.3	221		220	" "
132	367.8	193		192	C-1 Anthracene
		(263)			(Mixture)
133	369.7	217		216	C-1 Pyrene
134	371.5	233		232	Dimethyldihydropyrene
135	374.0	217		216	1-Methylpyrene
		233		232	Dimethyldihydropyrene
136	374.8	207		206	C-2 Anthracene
		223		222	C-3 Dihydrophenanthrene
137	377.7	207		206	C-2 Anthracene
		233		232	C-2 Dihydropyrene
138	381.4	207		206	C-2 Anthracene
139	383.8	231		230	Dimethylpyrene
140	386.2	231		230	2,7-Dimethyl or 1-ethylpyrene
141	390.1	207		206	C-2 Anthracene
		(248)			Mixture
142	398.4	--		--	Baseline
143	399.4	229		228	Chrysene
144	400.0	229		228	"
145	402.7	(229)		(228)	"
		261			

APPENDIX II-1. BATCH EXTRACTION PROCEDURES

a) Clathrate Only

Either 7.5 or 10.00 g of the appropriate coal was placed with a magnetic stirrer bar in a 400 ml Schlenk flask. The flask was introduced into the dry box in the normal manner (see Appendix II-10 for dry box procedure). The desired amount of $(NPr_4)(Al_2Et_6I)$.aromatic solvent liquid clathrate (100 ml for most extractions) was measured in a measuring cylinder and poured over the coal. With most coals the clathrate darkened immediately but there was no other signs of reaction. 100 ml of solvent (toluene, mixed xylene or tetralin), (freshly distilled and stored over molecular sieves) was then added. The flask was stoppered, removed from the dry box and placed in fumehood under a constant but slow flow of nitrogen. The flask was maintained at 70° in an oil bath for the desired time (usually either 4 hours or 20 hours) whilst the coal and the two phases were stirred. The mixture was allowed to cool under an excess pressure of nitrogen.

b) Catalyst

The procedure was as outlined in (a) until addition of the liquid clathrate. At this point the catalyst was introduced. If the catalyst was fully homogeneous and neutral then the desired amount was added before adding 100 ml of the liquid clathrate. If the catalyst was of the transition metal sustained type (i.e. homogeneous and 'locked in') then the desired volume was added to the coal and the $(NPr_4)(Al_2Et_6)$.solvent clathrate was added to make the total liquid clathrate volume 100 ml. The rest of the procedure was as for (a) unless hydrogen gas was to be present during the extraction (see below).

c) In situ Hydrogenation

If hydrogen gas was used during the extraction, the procedure would be followed as for (a) and (b) until the reaction flask was removed from the dry box. A constant stream of dried H_2 gas was passed through the mixture during the extraction (see Figure 1 for a schematic of apparatus; the approach is identical to that employed in the 1983-84 Report). After the desired time the flask was removed from the oil bath and allowed to cool under a constant H_2 pressure.

d) Autoclave Operation

The equipment used for all elevated pressure runs consists of the following:

(i) Aminco high pressure reaction vessel (stainless steel, internal dimensions 3 5/16" x 10", catalogue #41-4135).

(ii) Aminco high pressure shaking assembly.

(iii) Custom-made glass liner for (i). A schematic is given in Figure II-1.

(iv) Custom-made metal cage for (iii), a schematic of which is also given in Figure II-1.

Reaction temperatures are attained within 1 hr and are maintained to ±2°C using a thermostatic control. Reaction temperatures are monitored using thermocouple that is placed inside the reaction vessel. A cool-down period of 2 1/2 - 3 hours is necessary following the reaction period. After the cool-down period the reaction vessel is vented and then flushed several times with argon prior to removal of the reaction vessel contents. The glass bomb liner facilitates anaerobic

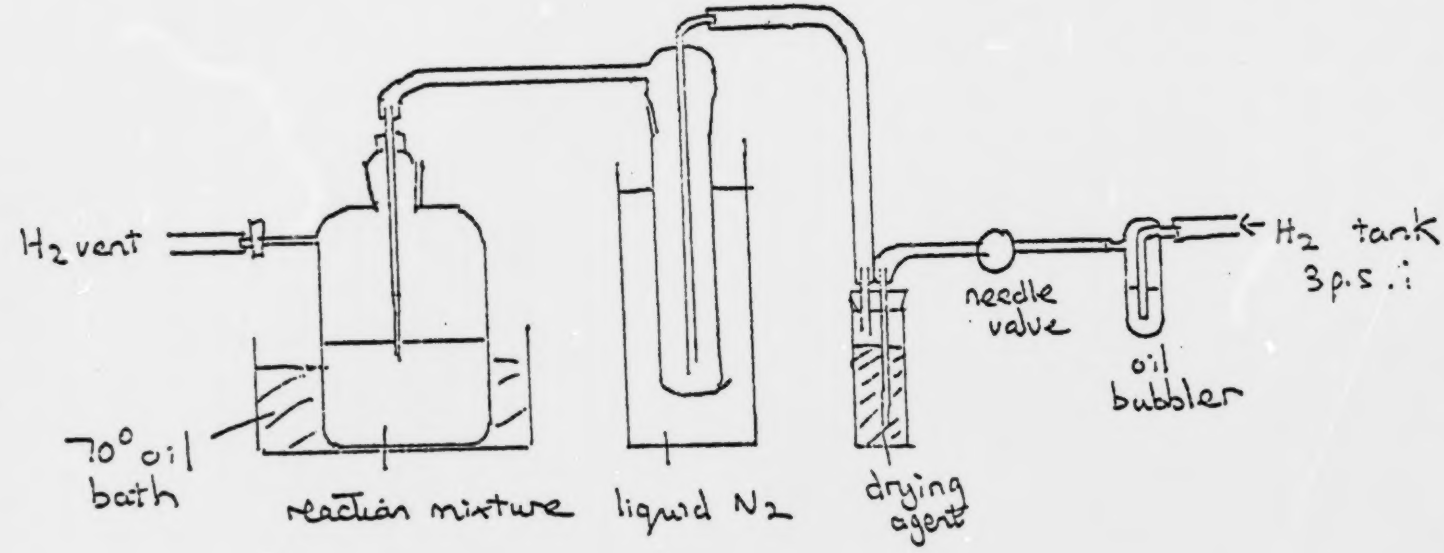


Figure 1. Schematic of Hydrogenation Apparatus

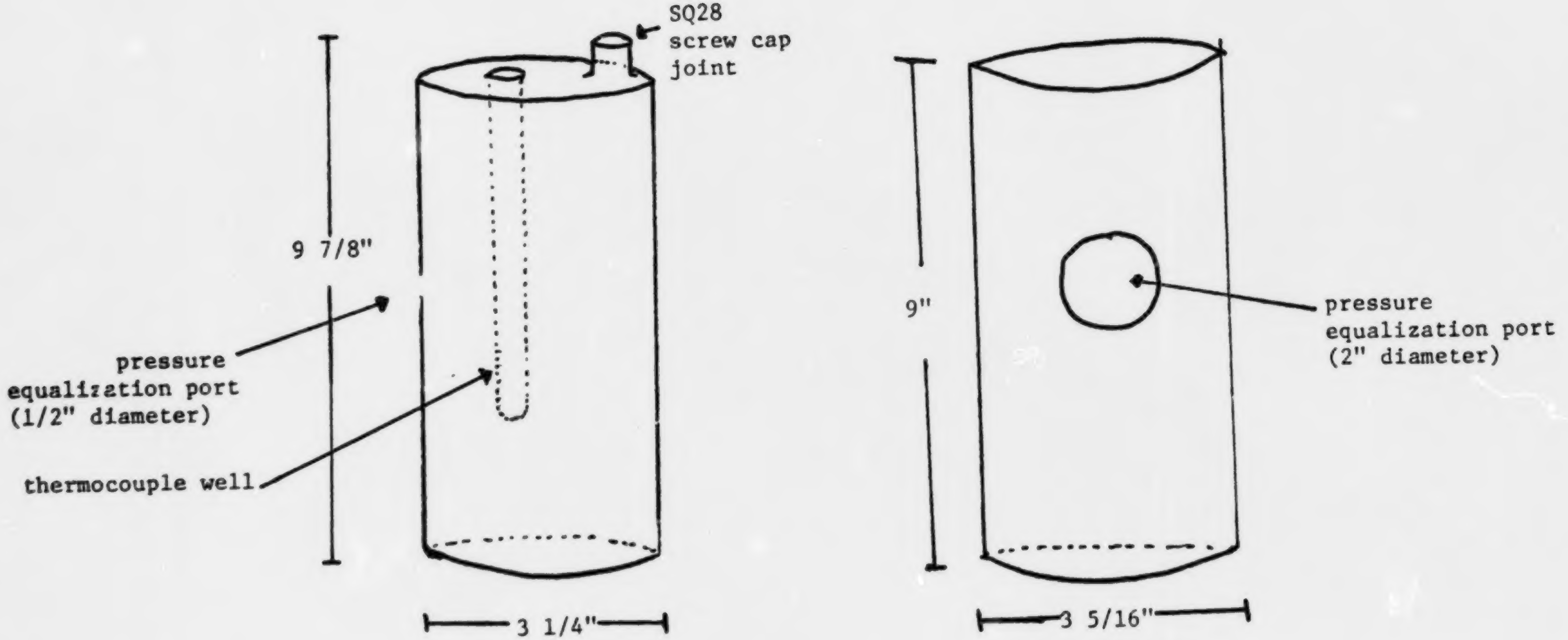


Figure II-1. Bomb liner and metal cage schematic.

transfer of the reaction materials between glovebox and bomb or vice versa.

APPENDIX II-2

METHODS FOR QUENCHING THE COAL/CLATHRATE SYSTEM

AND

SEPARATION OF MATERIALS

The following procedure is a modified version of that employed in the 1983-1984 Annual Report. The procedure outlined applies to both autoclave and ambient extractions.

The reaction mixture is first allowed to cool down to room temperature under an inert atmosphere (N_2 for ambient extractions, Ar for autoclave extractions). The reaction vessel is then placed inside a glove bag (N_2 atmosphere) and left to stand for 15-30 minmutes to allow settling of solid residue. The liquid phases (clathrate and aromatic) are decanted into a 250 ml beaker and left to stand for a further 5-10 minutes to permit complete separation of the liquid phases. The aromatic (upper) phase is decanted into a clean, dry 250 ml beaker and treated as described in (i) whereas the remaining clathrate phase is put into stoppered centrifuge tubes. Following centrifugation (10 minutes at 2500 rpm) the clathrate phase is decanted into a clean, dry 250 ml Erlenmeyer flask and stored under N_2 prior to workup (as described in (ii) below). The solid residue remaining in the centrifuge tubes is combined with the coal residue of the reaction vessel and worked-up as described in (iii). (i) Aromatic Phase:

The procedure is conducted under a nitrogen stream directed through a large plastic funnel. 20 ml of 10^{-4}M HCl is added to each 50 ml of aromatic in the flask. The acid is added slowly until the vigorous reaction ceases; it is then added more rapidly. After at least 15 minutes (all activity ceases) the mixture is filtered through a Buchner funnel.

The filter paper and cake are placed in a 50 ml beaker to dry. The filtrate is poured into a 250 ml separatory funnel (no grease is used). The flask is rinsed with distilled water which is added to the funnel. The aqueous layer is allowed to settle and is drained after which 20 ml of distilled water is added to the toluene. The funnel is shaken (three times with venting) and the water drained. The wash procedure is repeated five times. Bubbles or contaminants which adhere to the sides of the funnel are washed off with distilled water. The aromatic is transferred to a distillation flask (tared) and distilled (Appendix II-8).

After distillation of the aromatic, the flask is dried on the vacuum line ca. 1 day and then weighed. The contents of the flask are dissolved in chloroform-d and transferred to a 6-dram vial. The sample is frozen in the vial.

The inorganic residue from the acid wash is dried in a vacuum oven at 100°C overnight. The filter cake is allowed to cool in a dessicator, transferred to a 2 dram vial and stored.

(ii) Clathrate Phase:

The clathrate layer is poured slowly from a 250ml Erlenmeyer flask into a beaker which contains 1000 ml of 10% HCl mixed with ice. The HCl was stirred rapidly during the addition. When the reaction subsides 200 ml of chloroform is used to wash out the residue left in the Erlenmeyer flask and to dissolve the black organic material. The aqueous layer is decanted and the remainder filtered through a Buchner filter. The residue is transferred to the filter by rinsing with more chloroform as necessary. The residue cake is washed with 1000 ml of 10% HCl and chloroform; it is retained for pyridine extraction. The chloroform layers are treated as described below.

(iii) Coal Residue Phase:

The coal residue is transferred (using chloroform) from the reaction vessel to a beaker containing 1000 ml of 10% HCl ice/water solution, with rapid stirring. The residue is treated with chloroform and washed as for the clathrate phase.

The clathrate phase and coal residue treatments resulted in a chloroform solution and a solid residue from each. These were then treated as follows to extract the organic material.

a) Chloroform Solutions:

Two x 2000 ml solutions of cold/5% HCl are prepared (one for each chloroform fraction). All manipulations are carried out under a flood of nitrogen.

The chloroform/10% HCl mixture is placed in a 21 separatory funnel (no grease). The chloroform layer is run into an Erlenmeyer flask (about 800 ml of chloroform from the clathrate phase or 600 ml from the coal residue phase). The acid layer is discarded.

The chloroform solution is placed in a separatory funnel and shaken vigorously with 100C ml of 5% HCl. The shaking is repeated three times, with venting. The layers are allowed to separate and the chloroform layer run off (taking care to exclude solid material). The aqueous layer is discarded, the funnel rinsed and the wash of the chloroform layer with 1000 ml of HCl repeated. The chloroform layer is washed twice more with 500 ml portions of distilled water and slowly drained into a dry 1l wide-mouthed Erlenmeyer flask. Anhydrous sodium sulphate is added to cover the bottom of the flask (about 50 g). The flask is stoppered and swirled. The mixture is allowed to settle until no longer cloudy (approximately 10 minutes). The solution is filtered using a Buchner filter and all the sodium sulphate transferred to the funnel and washed with chloroform until the filter cake is white.

The chloroform is transferred with careful rinsing to a round bottom flask. The bulk of the chloroform is removed on a rotovap with a water bath of less than 50°C. When the volume is reduced to less than 50 ml, it is transferred to a tared round-bottom flask for distillation (Appendix II-8).

b) Solid Residues - Cold Pyridine Wash

The coal or clathrate residue is transferred to a 250 ml Erlenmeyer flask with a stirring bar. Working in a fumehood, 100 ml of dry pyridine is added to the flask and the mixture stirred for 30 minutes. The pyridine solution is decanted and filtered through a Buchner funnel using a pre-weighed filter paper. A further 50 ml of pyridine is used to re-extract the undissolved material left in the Erlenmeyer flask and this time both residue and pyridine are filtered, using the same Buchner funnel and filter paper. The residue is washed with small aliquots of dry pyridine until the filtrate appears clear. The filter is left running for ca. 30 minutes and the filter cake is washed with ca. 200 ml of 20% HCl in ordr to remove all pyridine. The filter cake and filter paper are dried in a vacuum oven at 60°C in a tared container until constant weight is achieved (1 - 2 days).

The filtrate is decanted slowly into 1500 ml of 15% HCl and stirred for 10 - 15 minutes. The resulting suspension is filtered through a pre-weighed filter paper 1 - 3 times until a clear solution is obtained. The solution is discarded and the filter cake is washed with 1000 ml of distilled H_2O and then dried in a vacuum oven at 60°C in a tared container until constant weight is achieved (1 - 2 days).

APPENDIX II-3.

NMR MEASUREMENTS: USE OF ARSENIC TRICHLORIDE AS A SOLVENT

For NMR measurements, 0.35 g of the pyridine extracted material was weighed into a tar ed vial and then 3 g of a solution containing 80% $AsCl_3$ and 20% $CDCl_3$ (v/v). Deuterated chlorofrm is added only as a convenient lock and reference; alternatively unlocked spectra may be obtained using 0.1% TMS as a reference, thus avoiding all interference in the 0-10δ region. For C^{13} measurements, the solution can be made 0.005 M in $Cr(AcAc)_3$ which acts as a paramagnetic relaxation agent. It is important to have a constant sample/solute ratio if comparative or quantitative studies are contemplated since the $Cr(AcAc)_3$ does give C^{13} signals. The vial was placed in a sonic bath for about 10 minutes. Since the $AsCl_3$ is water-sensitive and extra peaks have been observed in samples left in capped NMR tubes for 48 hours, the sample should be prepared just before it is to be measured. The sample tubes should be sealed using paraffin or polyethylene film to protect the sample from moisture during extended runs.

It is mandatory to perform all transfers in a fumehood and to wear protective gloves when handling $AsCl_3$. The toxic nature of this solvent should be recognized by workers adopting these procedures.

The proton and carbon 13 magnetic resonance spectra were recorded using a Bruker WM 250 MHz spectrometer operating at a field of 5.87 T. The quantitative C^{13} spectra were obtained at 62.87 MHz using inverse-gated decoupling (the decoupling was gated on only during acquisition) with a flip angle of 53 and a delay time of 5.0 s. The C^{13} shifts were measured relative to $CDCl_3$ at 77.0 ppm and the proton spectra were recorded at 250 MHz and were measured relative to $CDCl_3$ at 7.24 δ or TMS at 0.0 δ. Peak areas were integrated over fixed intervals after baseline adjustment.

APPENDIX II-4.

PREPARATION OF SAMPLES FOR MOLECULAR WEIGHT DETERMINATION

Approximately 0.5 grams of coal sample (accurately weighed) was added to 10 ml of dry pyridine in a glass vial with a ground glass stopper and sonicated until completely dissolved. Using a Pasteur pipette the sample plus a small amount of dry pyridine used to rinse the vial, was carefully pipetted onto an LH20 Sephadex column (approximately 80 g in pyridine) with a water jacket set at 60°C and eluted with dry pyridine. The column was kept under a stream of N_2 for the entire procedure. The work was performed in a fumehood and gloves were worn throughout.

The sample was collected in 10 ml fractions, beginning when the eluent had a faint yellow tinge, until it appeared almost colorless again (most of the ten fractions collected were dark brown). The graduated cylinders used for sample collection were rinsed with dry pyridine between fractions. 5 ml of each fraction was pipetted volumetrically into a labelled, clean, dry 125 ml Erlenmyer flask. This portion was used to determine the concentration of each fraction; the other 5 ml of the fraction was poured into a clean, dry volumetric flask and used subsequently for molecular weight determination by vapour phase osmometry (as described in Appendix II-5).

To determine the concentration of fractions, approximately 100 ml of 10% (v/v) HCl was added to the Erlenmyer flasks containing 5 ml portions of each fraction to precipitate the coal. This solution was then suction filtered through a labelled, clean, dry, tared filtering crucible using Whatman glass microfibre filters. Distilled water was used to thoroughly rinse the flasks and precipitate. The crucibles were evacuated overnight in a 60°C vacuum oven, cooled while still under vacuum and they reweighed. The results were used to calculate the concentration of coal in each fraction (grams of coal per kilogram of solvent) which is the C term in the equation for molecular weight determination by vapour phase osmometry.

Samples for spot average molecular weight determinations were prepared by weighing coal residues (just as they are after workup) on an analytical balance, transferring to 10 ml volumetric flasks and filling up to the mark with dry pyridine. Samples were prepared in triplicate in the range of 5 to 12 grams per kilogram of solvent.

APPENDIX II-5.

DETERMINATION OF MOLECULAR WEIGHT BY VAPOUR PHASE OSMOMETRY

Samples were prepared as described in the preceding section, Appendix II-4. When working with the samples and solvents, gloves were worn and work performed in the fumehood.

Standards were made with MW1580 polyethylene glycol standard of concentrations from 2 to 10 millimole/kg. The polyethylene glycol was weighed on an analytical balance to 4 decimal places and transferred to labelled 10 ml volumetric flasks. Dry pyridine was used to make the solution up to the mark.

A Hitachi Perkin-Elmer Model 115 Vapour Phase Osmometer was used and the instrument assembled for operation as described in the instrument manual. The operating temperatures were set a 36°C for the sub-oven and 41.5°C for the main oven for pyridine. Approximately 120 ml of pyridine was required to fill the thermistor block. This was added with a Pasteur pipette before assembly, allowing faster equilibration. Addition of solvent by the inject port is not recommended as the instrument does not equilibrate afterward.

Pyridine and samples were added to the injection syringes of the instrument with Pasteur pipettes. One-third turns of the injection knobs were used to deliver solvents and samples from the injection syringes to the thermistors.

The instrument must be equilibrated before samples were run (i.e. a 1/3 turn of the S.V. sampling knob produced deflection of the meter to the left of 0 only; and a 1/3 turn of the R.V. sampling knob produced deflection to the right of 0 only). The needle must return to rest at 0.

Measurement of the change in resistance of the thermistors (ΔR) were performed as directed in the instrument manual. At least 3 polyethylene glycol standards were made. If the values fitted the calibration curve, (see graph), then the unknown samples could be run. The slope may differ slightly but it must go through zero. If the values of ΔR do not fall on this line, the standards are remade or the trouble-shooting directions are followed in the instrument manual.

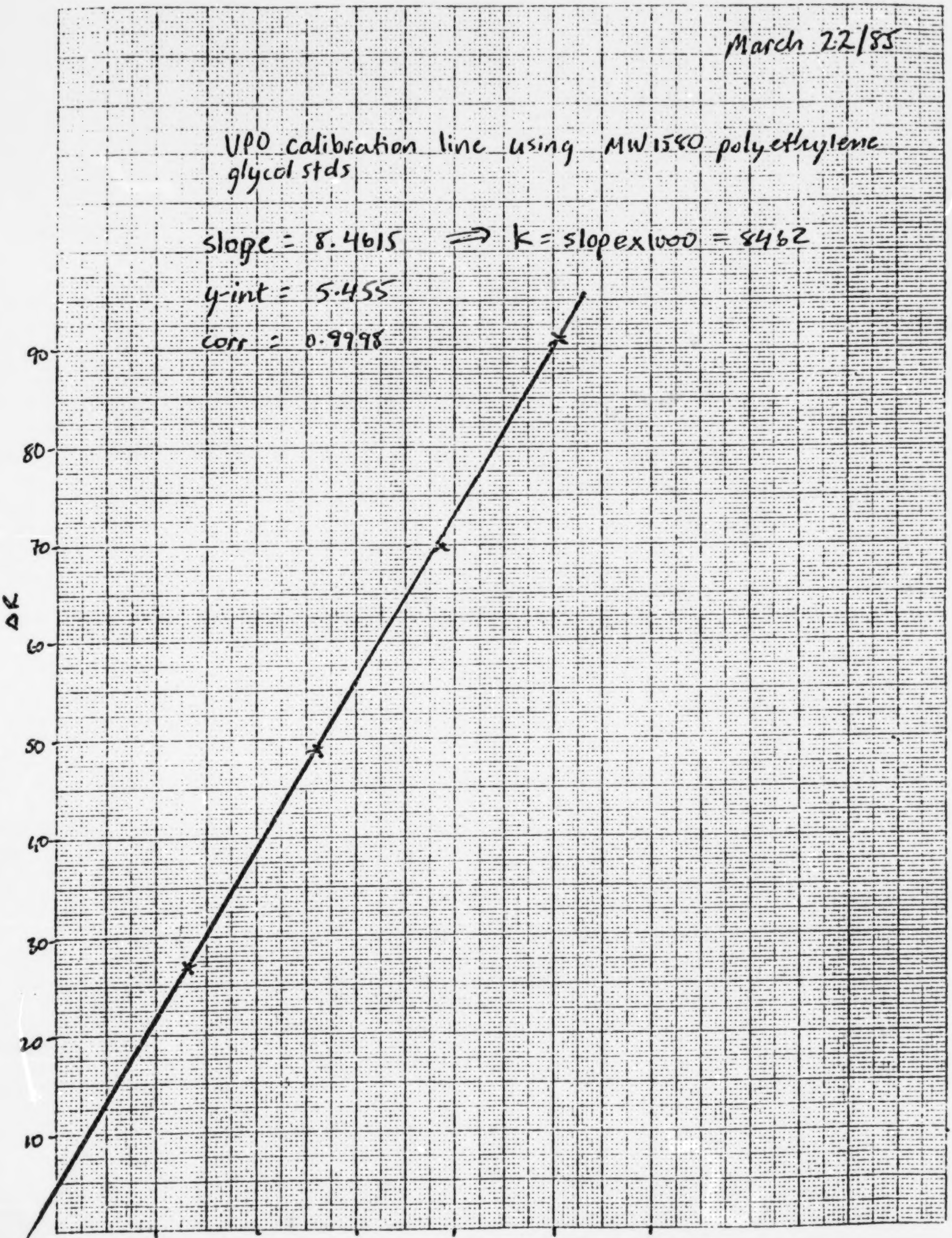
The instrument was best equilibrated, between 3 hours and 3 days after being turned on. If equilibration could not be reached, the termistor block was disassembled, dried out, 10 ml of benzene added, the block reassembled and turned on.

Calculations for $\Delta R/C$ and Mn were compeolted as in the instruction manual, i.e.

K (instrument constant) = slope of calibration graph x 1,000

Mn (molecular weight) = $\frac{K}{\Delta R/C}$ for each sample

K for graph given = 19,450 , therefore Mn = $\frac{19{,}450}{\Delta R/C}$



March 22/85

VPO calibration line using MW1580 polyethylene glycol stds

slope = 8.4615 ⇒ k = slope×1000 = 8462

y-int = 5.455

corr = 0.9998

☒ GRAPHIC CONTROLS CANADA LTD. MADE IN CANADA

G-14 SQUARE 10 X 10 TO THE CM SPECIFY TRACING OR DRAWING PAPER

RESULTS OF MW DETERMINATIONS

FOR 10-64C COLD PYRIDINE SOLUBLES

$k = 7945$ V_{1-8} are 10 ml fractions

	ΔR	$C(g.kg^{-1})$	Mn
V_1	0.0	0.000	--
V_2	5.5	3.088	4463
V_3	11.0	6.033	4365
V_4	12.0	6.912	4566
V_5	12.5	4.622	2943
V_6	10.5	2.556	1933
V_7	10.5	0.716	542
V_8	11.5	0.593	410

APPENDIX II-6.

GC/MS: SEP-PAK FRACTIONATION OF COAL LIQUIDS

Sep-Pak cartridges are mini-chromatography columns. Water Associates Sep-Pak (Part No. 51900) silica cartridges were used to fractionate the toluene or chloroform soluble fractions of the coal liquids. The sample could be fractionated by washing through the Sep-Pak with solvents of varying polarity. A mixture of dichloromethane and pentane in the ratio of 25/75 was found to preserve all of the GC volatile material in the sample while at the same time leaving the maximum amount of non GC-volatile material on the Sep-Pak.

The Sep-Pak was left in its sealed foil envelope until just before use. The sample, which had been stored in $CDCl_3$ was poured into a pre-weighed 100 ml round bottom flask. The vial was rinsed with CH_2Cl_2 and poured into the flask. The sample was taken to dryness on a rotary evaporator and the flask reweighed to determine the weight of the sample.

The sample was redissolved in approximately 2 ml of CH_2Cl_2/C_5H_{12}. A preweighed 50 ml round bottom flask with a B24 neck was placed in a 250 ml beaker. The Sep-Pak was removed from its envelope and the long end attached to the Luer lock of a 5 ml syringe. The Sep-Pak-syringe was held inside the 50 ml flask with the plunger removed. A clean Pasteur pipette with 1 ml bulb was used to transfer the sample into the syringe barrel. The sample flask was rinsed with CH_2Cl_2/C_5H_{12} and the rinse solution added to the syringe. The plunger was inserted into the syringe and the sample pushed through the Sep-Pak.

The syringe barrel was filled with the CH_2Cl_2/C_5H_{12} mixture and flushed through again. This was repeated until approximately 15 mls of solvent had been used or until the effluent from the Sep-Pak was very lightly coloured. The sample was taken to dryness on a rotary evaporator and weighed.

SAMPLE PREPARATION FOR GAS CHROMATOGRAPHY

The concentration desired for GC and GC/MS analysis was approximately 0.0150 g of dry sample per 2 mml of CH_2Cl_2; this gave a full-scale signal when 1 µl was injected at an attenuation of 32×10^{-12} on the Varian 2440 GC. The concentration of the sample after fractionation on the Sep-Pak, was adjusted to this range by adding the appropriate amount of CH_2Cl_2. The sample was ready for GC analysis and transferred to a Pierce 3.5 ml screw cap septum vial with 12 mm Pierce TufBond Teflon/Silicone disc.

GAS CHROMATOGRAPHIC ANALYSIS PROCEDURE

Gas chromatograms were recorded using a Varian 2440 gas chromatograph equipped with a flame ionization detector; a Hewlett-Packard 3390A Reporting Integrator was used in conjunction with the gas chromatograph (GC). The GC has been modified for use with capillary columns and to allow the sample to be injected directly on the column, to avoid possible pyrolysis in a heated injection block.

Analyses were conducted using a 30m x 0.22m(ID) WCOT fused silica capillary column with SE-54 liquid phase (Chromatographic Specialities). Helium was used as the carrier gas with a linear flow velocity of 60 cm/sec. Generally the sample concentrations were adjusted to bring the signal on scale with the attenuation set at 32 x 10^{-12}, such concentrations being appropriate for GC/MS analysis.

1 μl samples were injected directly on to the column with the column at 30°C. This temperature was held for 3 minutes and the temperature increased at 6°/minute to 290° where the temperature was held for approximately 20 minutes.

SAMPLE PREPARATION FOR GC/MS ANALYSIS

The sample was fractionated as described above and the concentration adjusted so that 1 μl at attenuation of 32 x 10^{-12} gave a full scale signal on the Varian 2440 GC. This concentration was suitable for GC/MS analysis.

For the GC/MS analysis an internal standard was added to the solution. The internal standard contained:

naphthalene;	signal appeared at 20.0 minutes*
phenanthrene;	signal appeared at 30.7 minutes*
anthracene:	signal appeared at 30.9 minutes*
chrysene;	signal appeared at 41.2 minutes*

*Retention times on Varian 2440 GC with conditions as described above.

APPENDIX II-7.

SYNTHESIS OF TRANSITION-METAL COMPLEXES

(a) Preparation of $[NR_4][Fe(CO)_4H]$.

The following route is based upon that described by N. N. Greenwood et al., J. Chem. Soc. (A), 1969, 2345.

$Fe(CO)_5$ (4.0 ml, 0.0298 mole) was stirred in 150 ml of concentrated NH_4OH for 24 hr, resulting in disappearance of the yellow $Fe(CO)_5$ phase and a discolouration of the NH_4OH phase to pinkish red. 0.0298 mole of the appropriate NR_4I (R = Me or Bu) salt was dissolved in the minimum amount of distilled water (150 ml) and added dropwise to the stirred solution resulting in the formation of a pink precipitate of $[NR_4][Fe(CO)_4H]$. Filtration, washing (2 x 50 ml, H_2O, 2 x 20 ml hexane) gave a purple-pink solid. Following vacuum drying yields of up to 20% were obtained.

Since $[NR_4][Fe(CO)_4H]$ salts are air sensitive even in the solid state all manipulations were carried out under an atmosphere of N_2. Characterization was conducted through ^1H NMR.

(b) Preparation of $HCo[P(OMe)_3]_4$

In a typical reaction 5.33g (18.3 mmole) of $Co(NO_3)_2 \cdot 6H_2O$ were dissolved in 100 ml of EtOH. The solution was stirred under N_2 at -78° to give a pink solution. 12 ml (101.5 mmole) of trimethylphosphite was added dropwise resulting in a colour change to purple. $NaBH_4$ (2g, 52.9 mmole) was added as a solid and the mixture was stirred for 2 hours, following which the reaction mixture was allowed to warm to room temperature. The resulting solution was bright yellow in colour and following solvent removal in vacuo the resulting residue was extracted with hexane.

The filtered hexane solution was reduced in volume and chromatographed on neutral alumina (2 x 20 cm column) using hexane/Et_2O as eluant. Following solvent removal 3.15g (5.66 mmole, 31%) of $HCo[P(OMe)_3]_4$ was obtained as a pale yellow solid (characterized via ^1H NMR).

Problems are encountered if ethanol is used as solvent since transesterification occurs with the trimethyl phosphite, resulting in isolation of the corresponding $P(OEt_3)$ complex.

(c) Preparation of $KCo[P(OMe)_3]_4$

3.15g of $HCo[P(Ome)_3]_4$ and 0.23g of KH were stirred in 100 ml of THF at 70°C under vacuum for 40 hr. During this time the white product slowly precipitated out of solution. The extremely air-sensitive product was filtered and dried in vacuo, at all times being kept away from O_2 or H_2O. The reactive nature of the product was not outlined in the literature, leading to early difficulties in handling which have now been resolved.

(d) Preparation of $(\eta^3\text{-allyl})Co[P(OMe)_3]_3$. (1)

The $KCo[P(OMe)_3]_4$ obtained from (b) was stirred in 50 ml of THF under N_2 and one equivalent of C_3H_5I was added dropwise. The mixture was then stirred at 20°C for 10 hrs with gradual discolouration of the solution from clear to orange being observed during the course of the reaction. Following solvent removal the residue was extracted with 50 ml of hexane and filtered to give a clear orange solution of (1). Solvent removal in vacuo gives a yellow orange solid, 1 (yield >75%).

Formation and Behaviour of $[(mesitylene)Mn(CO)_3]PF_6$. $AlEt_3$ based liquid clathrate.

1.61g of $[(mesitylene)Mn(CO)_3]PF_6$ was stirred under N_2 with 100 ml of toluene. Following addition of 2.18 ml of $AlEt_3$ (4 equivalents) the liquid clathrate effect was noted. After one day the toluene (upper) phase became yellow like the clathrate (lower) phase, and after one week both phases were black-red in appearance. An obvious reduction in volume of the clathrate phase had also occurred.

14 ml of 1-methylnaphthalene was added to this mixture and the system was then heated to 70°C and put under 1 atm. of H_2 for 20 hr. After this time the solution had reverted to its original yellow appearance but without reappearance of the clathrate phase. GC analysis of the yellow solution showed no evidence for presence of fully or partially hydrogenated 1-methylnaphthalene.

APPENDIX II-8.

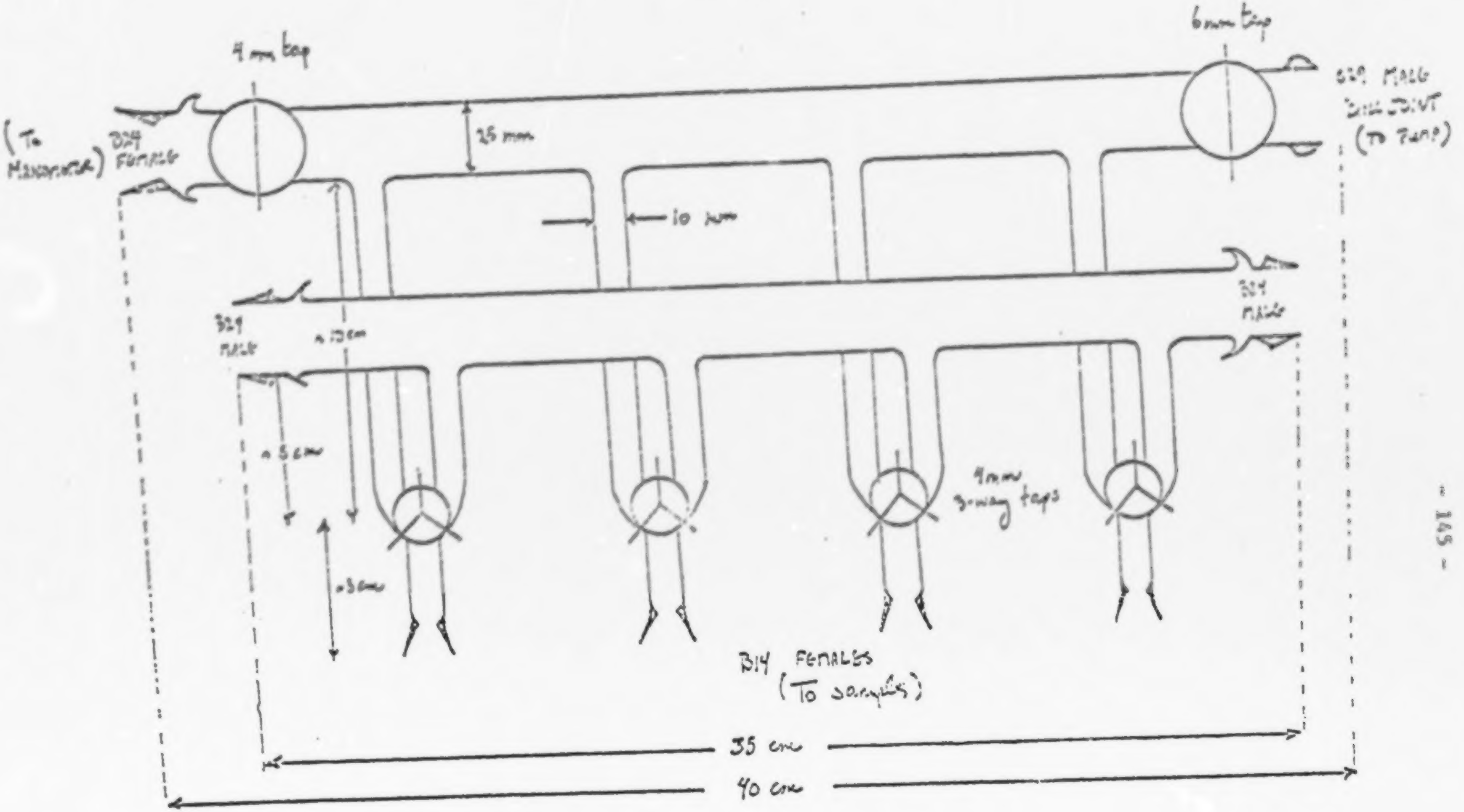
REMOVAL OF SOLVENTS BY VACUUM DISTILLATION

The Apparatus

The apparatus consisted of a vacuum pump, solvent trap, vaacuum/nitrogen manifold, nitrogen supply and distillation glassware.

The vacuum pump was a Precision Model D-25. Approximately 50 cm of 5/8" OD vacuum tubing connected the pump to the solvent trap. The sidearm of the trap was connected to the vacuum/nitrogen manifold (Figure 1). The 3-way valve of the manifold could be: closed, open to nitrogen or open to vacuum. The vacuum manifold was connected to the nitrogen manifold with 3/8" OD vacuum tubing. A needle valve controlled the flow of nitorgen which could be directed to flasks on the vacuum line or diverted from the system. The nitrogen manifold was connected via 1/4" OD tygon tubing to 2 x 250 ml Dreschel bottles, the second of which was half filled with glycerin to indicate nitrogen flow. The first Dreschel bottle (empty) provided a trap to prevent glycerin from entering the manifold. Each outlet on the vacuum manifold was connected to a 3-way valve via 1/4" OD vacuum tubing. A vacuum receiver adapter was connected to one valve via vacuum tubing. The tubing from another valve was connected to 1 metre of 1/4" OD rubber tubing. This served as the nitrogen bleed into the still pot.

The glassware included: a still head with B24 joints and B10 thermometer joint, a Fisher Scientific -10 to 360°C thermometer with B10 ground glass joint; B24 Liebeg condenser, vacuum receiver adapter with B24 joints and 500 ml round bottom receiver flask with B24 neck. The preparation of the sample is discussed below. Other equipment:



VACUUM/N_2 MANIFOLD.

Figure 1.

Vacuum/Nitrogen Manifold

Scale: 1cm = 2.0cm

a 250 Glas-col heating mantle, 1.4KVA voltage regulator, 2 o-rings, 2 clamps and one 21 metal bowl or pan with high sides.

Preparation of the Sample Flask

A modified Pasteur pipette was inserted into the sidearm of the distillation flask through a thermometer adapter to deliver a stream of N_2 into the sample during the course of the distillation. A Bunsen burner and long forceps were used to pull out the tip of a Pasteur pipette to a fine point. Several pipettes were prepared at one time as 5 per experiment were required.

A clean, dry, labelled 250 ml 2-neck (B19, B24) round bottom flask was pre-weighed for the distillation flask. The cap of a B19 thermometer adapter was unscrewed and the rubber washer removed. The washer was slid over the tip of the Pasteur pipette and pulled along its length until about 7 cm from the wide end. The thermometer adapter was inserted into the B19 neck (sidearm) of the flask. The pipette was inserted into the adapter and the rubber washer adjusted so that the tip of the pipette rested on the bottom of the flask. The lid was screwed on to the adapter and tightened.

Distillation Procedure

The distillation glassware was assembled as shown in Figure 2 and attached to the vacuum manifold. When the vacum line was not in use all valves on the manifold were closed. When setting up the distillation glassware the first step was to clamp the receiver flask to the metal support rods on the bench. It was clamped so that the bottom

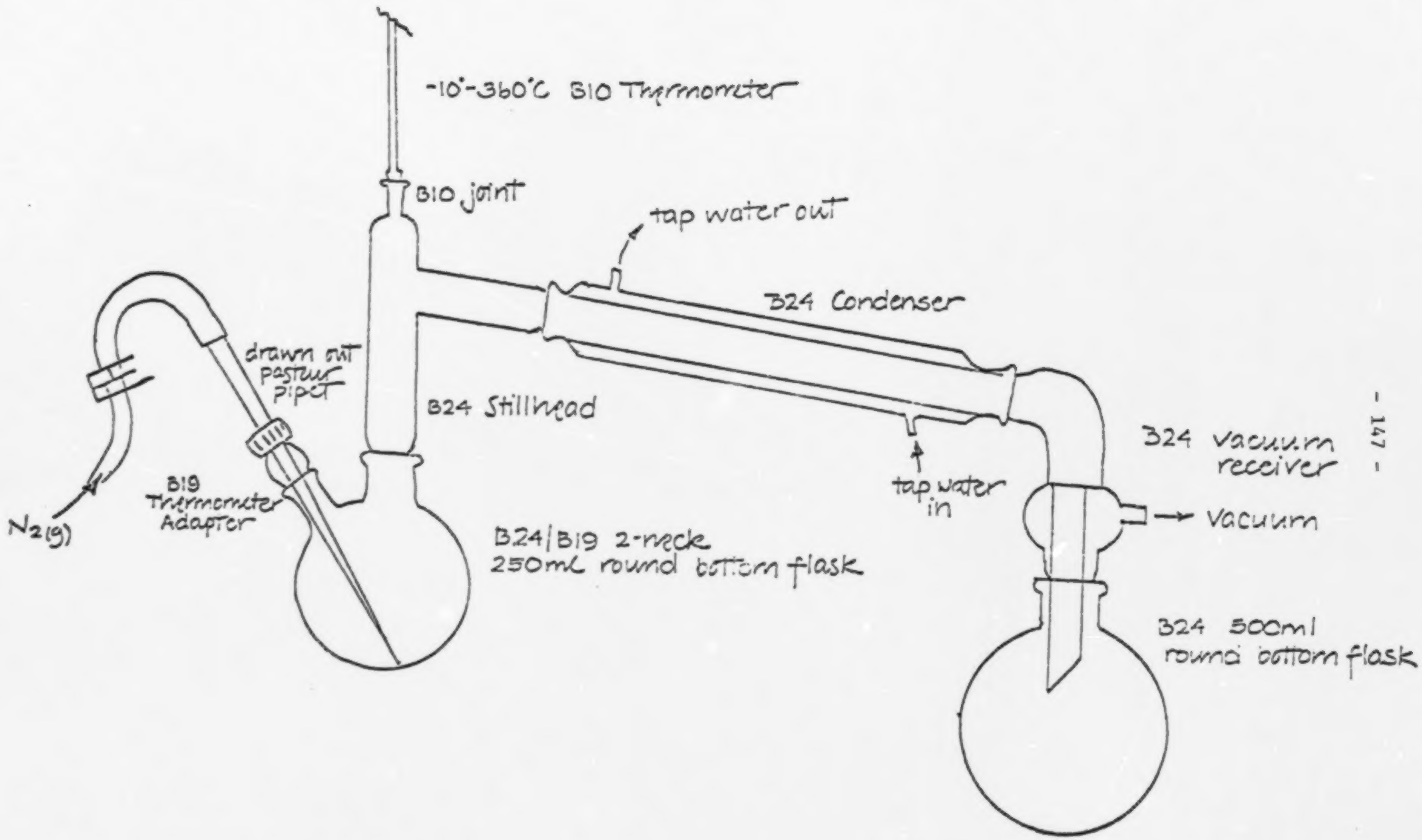


Figure 2.
Distillation Glassware

of the flask just touched the bottom of the metal bowl set under it. The bowl was filled with sufficient crushed dry ice to cover the flask. Acetone was poured into the bowl to form an acetone/dry ice slurry. The colder the receiver flask the less time the distillation took. Once the receiver flask began to cool, the flask containing sample was clamped to the metal support beams. (Because of the angles in the glassware the sample flask should be about 15 cm higher than the receiver flask.) The vacuum receiver adapter sat in the receiver flask and a cold water condenser was inserted into the adapter. The nitrogen bleed was opened and the tubing slipped over the end of the Pasteur pipette. To control the rate of N_2 delivery a tubing clamp was tightened n the nitrogen line until bubbling in the flask was barely discernible.

With the vent on the vacuum manifold closed the vacuum pump was started. A Dewar flask half filled with liquid nitrogen was placed over the trap and supported by an o-ring clamped to the metal rods. The Dewar flask was then topped up with nitrogen. The valve to the receiver adapter was opened slowly to vacuum. When the system was evacuated the sample began to bubble vigorously. The vacuum and flow of nitrogen were adjusted so that the sample bubbled but did not splash and the flask began to cool. If the vacuum was too great the sample "bumped" over to the receiver flask. When vacuum and nitrogen bleed were adjusted, the heating mantle was set under the flask and held in place by an o-ring clamped to the support rods. The voltage regulator on the heating mantle was turned on, set at slightly less than 30.

The distillation was checked periodically to ensure the correct vacuum/nitrogen ratio for maximum efficiency. This was determined by a slow, even bubbling of the sample being distilled.

Vacuum distillation of the toluene (A) fraction took approximately 30 minutes, the chloroform fractions (B and C) 20 minutes and the cold pyridine fractions 1 hour 30 minutes to 2 hours.

When the solvent had been distilled the heating mantle was removed and the valve to the vacuum line closed. The flow of nitrogen was increased at the needle valve and the tubing clamp slowly opened until the system filled with nitrogen to atmospheric pressure. The flow of nitrogen was decreased and the valve closed. The rubber tubing was removed from the pipette and the flask removed from the distillation apparatus. The flask containing sample was weighed when it came to room temperature.

PURIFYING AND DRYING OF SOLVENTS

Approximately 4 g of sodium metal, wiped free of mineral oil and cut into small pieces, was added to 500 ml of toluene in a 1 litre flask. Approximately 3 g of benzophenone was added to act as an indicator when the toluene was dry. Another 500 ml of wet toluene was added to the flask and the flask set into a 1000 ml, 500 watt Thermowell heating mantle connected to an Armaco 1.4 KVA voltage regulator set at 80. A reflux/collecting apparatus with a 500 ml collecting bulb was set up. After filling the still and before turning it on, the system was flushed with nitrogen for about 2 minutes after which the flow was decreased and the reflux begun. After refluxing for approximately 1 hour 30 minutes, the indicator turned blue signifying that the toluene was dry and ready for distillation.

If the toluene still was used every day, after about one month sodium oxides formed in the bottom of the 1 litre flask and the colour of the indicator was always brown. White particles and a dark brown-black-colour when boiling indicated that the still needed cleaning.

The pyridine was dried and purified by reflux and distillation after adding about 3 g of sodium hydroxide to the wet pyridine. The still was set up in a fumehood and the voltage regulator set at 90. There was no colour indicator in the flask but after refluxing for 1 hour and 30 minutes the pyridine was dry and ready to be distilled.

APPENDIX II-9.

MEASUREMENT OF LOSS ON IGNITION

Porcelain crucibles were ignited at 550°C for 1 hour, allowed to cool in a dessicator and weighed. Suitable amounts of sample were added to the crucibles and the weights recorded again to determine the amount of sample added to each. The crucibles were put into the pre-heated electric muffle furnace and ignited at 550°C for 1.5 hours. They were then placed in the dessicator, allowed to cool to room temperature and weighed again. The % ash and loss on ignition were then calculated. Watch glasses were placed over the crucibles when they were placed in the dessicator, so that the ash would not blow out when the cooled dessicator was opened with the accompanying rush of air.

APPENDIX II-10.

INERT ATMOSPHERE GLOVE BOX OPERATION

The pyrophoric nature of triethylaluminum requires that it be stored and manipulated under rigorously oxygen and water free conditions. All liquid clathrate manipulations were conducted in an inert atmosphere glove box (a Vacuum Atmospheres Corporation HE-93-B-I model glove box obtained on loan from B.C. Research). Prepurified grade nitrogen was further purified by continuously recycling through oxygen and water scrubbers. The oxygen scrubber was regenerated daily using 6% hydrogen in nitrogen.

All materials were introduced to the dry box through an antechamber. The antechamber was evacuated for 5 minutes, refilled with pure nitrogen, and then evacuated for a further 10 minutes before any materials were introduced to the glove box.

APPENDIX III-1.

REVIEW OF OBJECTIVES

Since the initial proposal December 1981, the principal objectives of the programme have remained in force, namely:

(1) To investigate the dissolution of coal solid at room temperature and pressure in a novel solvent system designated "liquid clathrate".

(2) To investigate the efficiency of stripping coal liquid from the "liquid clathrate" phase with solvent.

(3) To determine the efficiency of the process for high and medium volatile bituminous and for sub-bituminous Western Canadian coals.

(4) To characterize the physical and chemical properties of hydrocarbon product from the above multi-phase processes.

(5) To evaluate clathrating media that incorporate hydrogenation catalysts for in situ upgrading in the coal liquefaction process.

(6) To apply clathrated catalysts to upgrading of heavy liquid fuels of diverse type.

In the light of the above, we proposed a programme of work summarized into two phases as follows:

PHASE I

(i) Liquefaction of well-characterized B.C. coals is evaluated employing established clathrate systems. Yields in both the solvent and liquid clathrate phases to be determined.

(ii) Comparison of coal liquid quality and yield wih high temperature liquefaction product to be made.

(iii) New clathrate and collector solvent combinations that are low cost and air/water stable to be developed.

PHASE II

(i) *In situ* upgrading by clathrate compatible homogeneous catalysts at one atmosphere of hydrogen to be undertaken.

(ii) Homogeneous catalyst/clathrate combinations to be developed with reference to efficiency, cost and stability.

(iii) Application of homogeneous cataysts to heavy liquid fuels using the liquid clathrate/collector solvent combination.

(iv) Quality of upgraded liquid to be tested by standard analytical procedures and volatility.

(v) Characterization of the coal liquids to be undertaken in terms of their aromaticity, polarity and molecular weight using a variety of spectroscopic and analytical techniques.

APPENDIX III-2

Modified Brown-Ladner Equations

I. Schwager, Farmanian and T. F. Yen

$$f_a = \frac{\frac{C}{H} - \frac{H_\alpha^*}{x} - \frac{H_o^*}{y}}{\frac{C}{H}}$$ = fraction of total carbon which is aromatic carbon

$$\frac{H_{aru}}{C_{ar}} = \frac{\frac{H_\alpha^*}{x} + H_{ar}^* + \frac{O-O_{OH}}{H}}{\frac{C}{H} - \frac{H_\alpha^*}{x} - \frac{H_o^*}{y}}$$ = ratio of substitutable aromatic edge atoms to total aromatic atoms

$$\sigma = \frac{\frac{H_\alpha^*}{x} + \frac{O}{H}}{H_{ar}^* + \frac{H_\alpha^*}{x} + \frac{O-O_{OH}}{H}}$$ = fraction of the available aromatic edge atoms occupied by substituents

$$R_s = \sigma C_A \frac{H_{aru}}{C_{ar}}$$ = number of substituted aromatic ring carbons

$$n = \frac{H_o^*}{H_\alpha^*} + 1$$ = number of carbon atoms per saturated substituent

$$C_A = \frac{f_a (C)(M)}{100}$$ = total number of aromatic carbon atoms

$$R_A = C_A \left(\frac{1 - H_{aru}/C_{ar}}{2} \right) + 1$$ = number of aromatic rings

C = mol % carbon

H = mol % hydrogen

O = mol % oxygen

O_{OH} = mol % phenolic oxygen

H_{ar}^{*} = mol fraction aromatic hydrogen ($> 5.0\delta$)

H_{α}^{*} = mol fraction hydrogen α to aromatic ring ($<5.0 >1.73\delta$)

H_{o}^{*} = mol fraction of aliphatic hydrogen not α to aryl ring ($< 1.73\delta$)

x = average ratio of hydrogen to carbon on carbons α to aryl ring

y = average ratio of hydrogen to carbon on aliphatic carbons not α to aryl ring

Assumptions: All oxygen is attached to aryl rings in either phenol or aryl ether groups. All phenolic hydrogens found by the TMS derivative method are under the aryl absoprtion. $x = y = 2$.

Reference III-2-1.

II. Bartle and Jones

$H_{\alpha}^{*} = \frac{H_{\alpha}}{H}$ where $H_{\alpha} = 2 - 3.3\ \delta$

replaces $H_{\alpha} = <5.0 >1.73\ \delta$

$H_{\beta}^{*} = \frac{H_{\beta}}{H}$ where $H_{\beta} = 1.0 - 1.6\ \delta$

replaces $H_{o} = <1.73\ \delta$

$H_{ar}^{*} = \frac{H_{ar}}{H}$ where H_{ar} = 5.5 - 9.0 δ with assumption 60% of the hydrogen is phenolic

The Brown-Ladner approach is then applied with these modifications

III. f_a^{*} = fraction of total carbon which is aromatic based on ^{13}C spectra.

Reference III-2-2.

II-2-1. I. Schwager, P. A. Formanian and T. F. Yen, in Analytical Chemistry of Liquid Fuel Sources: Tar Sands, Oil Shale Coal and Petroleum. P. C. Udena, S. Siggia and H. B. Jensen editors. Adv. in Chemistry 170 American Chemical Society, Washington (1978), p. 66.

II-2-2. K. D. Bartle and D. W. Jones in Analytical Methods for Coal and Coal Products, Vol. II, Clarence Karr Jr. editor, Academic Press, New York, 1978, p. 134.

APPENDIX III-3.

Application of $AsCl_3$ as Solvent References

1) H.L. Retcofsky & T.A. Link in Analytical Methods for Coal and Coal Products, C. Karr Jr. ed., Volume II, Academic Press Inc., New York, 1978, p161.

2) H.A. Szymanski, A. Bluemle and W. Collins, Appl. Spectr., 19, 137 (1965).

3) H.A. Szymanski and A. Bluemle, J. Polym. Sc., Part A, 3, 63 (1965).

4) A.K. Bose, M. Sugiura and P.R. Srinivasan, Tetrahedron Letters, 14, 1251 (1975).

5) C.G. Collins, E.W. Hagaman, R.M Jones and V.F. Rosen, Fuel, 60, 359 (1981).

6) T.G. Squires, C.G. Venier, J.D. Hunt, J.C. Shei and B.F. Smith, Fuel, 61, 1170 (1982).

7) G. Erbatur, A.F. Gaines, M. Ali Hoscan, Y. Yuram, S. Icli and T. Wirthin, Fuel, 58, 121 (1979).

8) K. Ouchi, K. Tanimoto, M. Makobe and H. Iton, Fuel, 62, 1227 (1983).

9) N.E. Cooke and R.P. Gaikwad, Fuel, 63, 1468 (1984).

10) J.A. Franz, D.M. Camaioni and W.E. Skiens in Coal Structure, M.L. Gobarty and K. Ouchi editors, Advances in Chemistry Series 192, American Chemical Society, Washington D.C., 1981, p75.

11) D.J. Cookson and B.E. Smith, Fuel, 61, 1007 (1982).

12) H.L. Retcofsky, F.K. Schweighardt and M. Hough, Anal. Chem., 49, 585 (1977).

13) J.K. Brown and W.R. Ladner, Fuel, 39, 87 (1960).

14) I. Schwager, P.A. Farmanian and T.F. Yen in Analytical Chemistry of Liquid Fuel Sources: Oil shale, Coal and Petroleum, P.C. Udena, S. Siggia and H.B. Jensen editors, Advances in Chemistry Series 170, American Chemical Society, Washington D.C., 1978, p66.

15) K.D. Bartle and D.W. Jones in Analytical Methods for Coal and Coal Products, C. Karr Jr. editor, Academic Press Inc., New York, 1978, p103.

16) C.E. Snape, W.R. Ladner and K.D. Bartle, Anal. Chem., 51, 2189 (1979).

17) M.I. Burger, Fuel, 63, 1621 (1984).